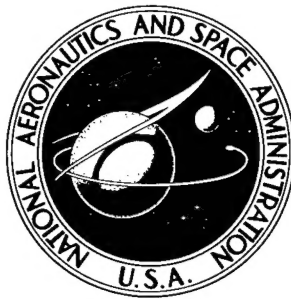


NASA TECHNICAL NOTE




NASA TN D-2493

NASA TN D-2493

PROPERTY OF:

ADPTIC LIBRARY

  
**DISTRIBUTION STATEMENT A**  
Approved for Public Release  
Distribution Unlimited

57263

**EVALUATION OF SELECTED REFRACTORY  
OXIDE MATERIALS FOR USE  
IN HIGH-TEMPERATURE PEBBLE-BED  
WIND-TUNNEL HEAT EXCHANGERS**

*by John D. Buckley and Bennie W. Cocke, Jr.*

*Langley Research Center  
Langley Station, Hampton, Va.*

**20011129 090**

EVALUATION OF SELECTED REFRACTORY OXIDE MATERIALS FOR  
USE IN HIGH-TEMPERATURE PEBBLE-BED  
WIND-TUNNEL HEAT EXCHANGERS

By John D. Buckley and Bennie W. Cocke, Jr.

Langley Research Center  
Langley Station, Hampton, Va.

**Reproduced From  
Best Available Copy**

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

---

For sale by the Office of Technical Services, Department of Commerce,  
Washington, D.C. 20230 -- Price \$0.75

EVALUATION OF SELECTED REFRACTORY OXIDE MATERIALS FOR  
USE IN HIGH-TEMPERATURE PEBBLE-BED  
WIND-TUNNEL HEAT EXCHANGERS

By John D. Buckley and Bennie W. Cocke, Jr.  
Langley Research Center

SUMMARY

A test program has been carried out to evaluate several commercially available ceramic oxide refractory materials considered promising for use in 3000° F to 5000° F pebble-bed air heaters. Results are presented from comparative tests in laboratory kilns on the high-temperature properties of several types of zirconia, thoria, magnesia, and alumina materials. A discussion of materials selection for pebble-bed heat-exchanger construction is presented based on the aforementioned tests and operational experience with heat exchangers. *end*

The results of this program indicate that alumina is the most desirable refractory for use at temperatures below approximately 3400° F and calcia-stabilized zirconia appears most desirable for use at the higher temperatures. Loss of compressive strength at high temperature limits the maximum temperature for zirconia usage to approximately 4100° F. Tests of several types of zirconia materials showed a wide variation in properties such as crystal stability and thermal-shock resistance; thus, there is a need to test and select different types of zirconia for different environmental regions in a heat exchanger. The materials thoria and magnesia are considered inferior to zirconia for use in a 4000° F heat exchanger. *end*

INTRODUCTION

*TR* The need for high-temperature ground facilities for research on materials and heat-transfer problems associated with reentry and hypersonic flight led to a program at the NASA Langley Research Center to develop high Mach number test facilities using ceramic pebble-bed heat exchangers to supply high-temperature air. Under this program heat exchangers were constructed and operated at temperatures to over 4000° F by using calcia-stabilized fused-grain zirconia refractory linings and pebble beds. Initial operation of these facilities described in reference 1 was successful; however, problems developed with the zirconia materials in certain regions of the heat exchangers. Thermal shock of the refractory lining and compacting of the pebble bed were problems in the high-temperature zones and, in addition, a serious decomposition of the zirconia *end* →

[material identified as inversion] (see ref. 2) [occurred at lower temperature regions in the lining and bed of the heat exchanger.]

Since very limited data were available on the properties of zirconia and other high-temperature refractory oxide materials at elevated temperatures and under the type of cyclic heating environment imposed by exchanger operation, a program was undertaken to define, on a direct comparative basis, the properties of several refractory oxide materials available for possible use in heat exchangers at temperatures above 3000° F.]

In this program, [the materials chosen for evaluation were stabilized zirconia of several types, thoria, magnesia, and alumina. The program conducted was limited to the objective of determining the suitability of the various materials for use in the cycling heat exchanger which is capable of temperatures from 3000° F to 5000° F. Tests were designed to determine the comparative thermal-shock resistance, static load, and crystalline stability properties under cycling temperatures for refractory brick of the stated materials. Also included were tests to evaluate the critical temperatures for reactions at the interface between the various materials if used in contact in the design of a heat exchanger.] 5

This report presents the results of tests conducted under this program and includes data obtained in laboratory test kilns, and some data obtained by observation of material behavior in the actual heat exchanger. The suitability of the various materials for heat-exchanger use is discussed.

## PROBLEM AND TEST APPROACH

### Ceramic Heat-Exchanger Problem Areas

A typical ceramic heat exchanger used to produce high-temperature air for a blowdown jet or wind tunnel is illustrated in figure 1. It consists of a steel pressure vessel which is lined with insulating and refractory ceramics and partially filled in its center core with a porous bed of 3/8-inch-diameter ceramic pebbles for heat storage. A burner is provided for heating the pebble bed and a water-cooled nozzle is located at the top to provide a test region for models. In operation the burner is fired by using propane and air with oxygen enrichment and the exhaust gases pass down through the porous bed until the desired temperatures are reached in the bed; the burner and exhaust are then closed off and high-pressure air is brought in at the bottom and passes through the heated pebble bed and out through the water-cooled nozzle to give the desired heated airstream for tests. Details of design and operation of this heat exchanger are discussed in reference 1.

A typical heat-exchanger operation subjects the ceramic lining and pebble-bed materials to a temperature-cycling environment in which the maximum temperatures and heating rates are determined by operating techniques for the individual facility. The static load conditions on various components of the refractory materials are fixed by design. In the initial operation of the subject heat exchanger using partially calcia-stabilized zirconia refractory liner brick and .

pebbles, three basic problem areas were noted, a different material property being most significant in each respective area. In area A (fig. 1) where the burner flame is a maximum during heating, thermal-shock resistance is of prime importance in the refractory brick work and top layers of the pebble bed; area B is a 3000° F to 4000° F temperature zone and load capability becomes critical at a depth in the bed where loss of strength at elevated temperature may cause compacting of the pebbles due to plastic deformation and thus loss of bed porosity; the third area designated C and described in figure 1 by the band running at varying depths within the liner wall is a moderate temperature (approximately 2100° F maximum) region where inversion (crystalline instability discussed in ref. 2) caused crumbling of the calcia-stabilized zirconia used in the initial operation of the facility. Examples of the types of ceramic damage are shown in figure 2.

### Materials Evaluated

The consideration of materials for use in the 3000° F to 5000° F air heater limits the choice of materials to commercial oxides with melting points over 3000° F. Tests were therefore limited to known and available materials meeting these conditions and included zirconia manufactured in several ways, thoria, magnesia, and alumina. The general properties and normal melting temperatures as published in general literature for these refractory oxides are shown in table I. As shown, the various zirconia products differed primarily in the degree and type of material used to gain crystalline stability in the material. Three types of calcia-stabilized zirconia were tested and two types using the rare earths ceria and yttria for stabilization were tested. As shown, tests were limited to one type of thoria, magnesia, and alumina.

TABLE I.- REFRACTORY MATERIALS EVALUATED

[Theoretical values obtained from reference 3]

Material	Chemical symbol and characteristics	Theoretical values		
		Melting temperature, °F	Thermal conductivity	Specific gravity
Zirconia A	ZrO <sub>2</sub> - fused grain, partially stabilized with calcia	4900	14.3 at 2400° F	5.6
Zirconia B	ZrO <sub>2</sub> - fused grain, fully stabilized with calcia	4800	14.3 at 2400° F	5.6
Zirconia C	ZrO <sub>2</sub> - fused grain, partially stabilized with ceria	4200	14.3 at 2400° F	5.6
Zirconia D	ZrO <sub>2</sub> - sintered, partially stabilized with calcia	4900	14.3 at 2400° F	5.6
Zirconia E	ZrO <sub>2</sub> - sintered, partially stabilized with yttria	4700	14.3 at 2400° F	5.6
Thoria	ThO <sub>2</sub> - high purity	5975	14.0 at 2400° F	10.0
Magnesia	MgO - high purity	5075	40.8 at 2012° F	3.57
Alumina	Al <sub>2</sub> O <sub>3</sub> - high purity	3700	30.0 at 2400° F	4.0

## Test Methods

Tests under this program were designed to evaluate the available refractory products in terms of the properties required for use in the critical regions discussed, that is, these tests simulated as closely as possible the environment of the critical zones of the heat exchanger. Since operating experience with fused-grain partially stabilized zirconia was available, all tests were conducted on a direct comparative basis with this material. In addition, tests were included to determine the compatibility of the various ceramics in contact at elevated temperatures. The following tests were made: (a) thermal shock, (b) high-temperature load, (c) crystalline stability, and (d) reaction temperature. All tests for thermal-shock and high-temperature load capability were made in the zirconia lined test kiln with samples set on pallets of the test materials to minimize effects of possible reactions between materials.

Thermal-shock tests.- Thermal-shock resistance of the various materials was determined by heating test samples in brick in an oxyacetylene-fired test kiln constructed with a zirconia refractory as shown in figure 3. For these tests, bricks of each material type being evaluated were placed in the kiln with a brick of the fused-grain partially stabilized zirconia type (hereafter referred to as standard zirconia A) and arranged so that the torch flame would impinge the front faces of the bricks (fig. 4) as in the ceramic heater usage. Brick specimens used for most tests were typical heat-exchanger shapes with tongue and groove joints as shown in figure 4. For two of the test materials, standard shapes were not available and specimens of comparable size and shape were cut from basic straight brick. In a typical single-cycle test, the top of the kiln would be closed and the torch fired at a fixed firing rate until the samples reached a temperature of approximately  $4000^{\circ}\text{F}$  as determined from an optical pyrometer viewing the samples through the side viewing port. The torch was then shut off and the samples were allowed to cool to ambient conditions for examination. For multiple cycle tests, the torch was refired when the samples cooled to approximately  $3000^{\circ}\text{F}$  in each cycle to more nearly represent the heat-exchanger operation as a continuously fired facility. Kiln firing rates for these tests required approximately 30 minutes to heat from ambient to  $3000^{\circ}\text{F}$  and approximately 1 hour to heat from  $3000^{\circ}\text{F}$  to  $4000^{\circ}\text{F}$ . All tests were limited to a maximum temperature of  $4100^{\circ}\text{F}$  by the capabilities of the test kiln.

High-temperature static-load evaluation.- The basic load capability of the refractory products was evaluated at temperatures between approximately  $3400^{\circ}\text{F}$  and  $4000^{\circ}\text{F}$  by heating 1-inch cubes of the individual materials under a static load in the oxyacetylene kiln. Figure 5 illustrates the typical manner of arranging a test cube under weight in the kiln chamber and figure 3 shows the kiln with the top closed and a loading weight protruding through a chimney opening in the top. A typical test consisted of heating the cube under the chosen weight and recording the temperature at which the load column significantly slumped due to cube failure at the specific load. Cube temperature as a function of time during heating was monitored by an optical pyrometer on each test. The tests at various loadings were accomplished as separate tests with new cubes and loading weights used for each test. Loading weights were observed after each test to insure that no deformation of the loading train had occurred.

Each test condition was repeated at least twice for a check on repeatability of test technique. In typical test cycles the cube was heated to 3000° F in approximately 1 hour and then the temperature was increased at a rate of approximately 30° F per minute until failure occurred.

Evaluation of crystal stability.- The crystal structure of zirconia (discussed in refs. 2 and 4) makes this material subject to structural breakdown because of a crystal inversion which occurs when the material is heated to the characteristic temperature range from 1500° F to 2100° F. The zirconia materials used in this program each had been manufactured with additives such as calcia or the rare earth oxides to stabilize the crystal structure and the zirconia products were considered to be free of the tendency of inversion breakdown. An evaluation of the effect of low-temperature (1500° F to 2100° F) cycling on the strength of the various zirconia materials was conducted, however, to determine the degree of stabilization achieved. This evaluation was made by subjecting pebbles and cubes from different zirconia brick to repeated heating cycles between 1100° F and approximately 2100° F. These tests were conducted in an electric heat-treat furnace (fig. 6) which was programed to heat and cool automatically between the temperature limits desired. Temperature time histories for each cycle (heat to 2100° F and cool to 1100° F) were recorded on a Brown recorder connected for continuous temperature sampling. Cooling phases were accomplished with the furnace closed and heating rates were chosen to give slow cycles (approximately 4 hours/cycle) as similar as possible to the heater environment.

The procedure in a typical test for strength loss due to thermal cycling consisted of subjecting the test material to 25 to 50 cycles of heating in the furnace and then measuring the cold crushing strength of the cube or pebble in a dynamometer with load application rate maintained constant for all tests.

Reaction temperatures for dissimilar refractories in contact.- The tendency for the various refractories to react (eutectic formation) when in contact at elevated temperatures was studied from the viewpoint of defining the maximum temperatures at which the various materials could be utilized in heat-exchanger construction without having damaging reactions at the contacting surfaces. Tests were conducted by placing the various combinations of ceramics in the oxyacetylene-fired kiln with surfaces in contact under moderate loadings (1/2 to 6 pounds per square inch) and firing the materials to progressively higher temperatures until the temperature for a damaging reaction at the contacting surfaces was defined. For some materials, additional tests were made to define the effects of loading and time on the extent of reaction between the subject materials.

## [RESULTS] AND DISCUSSION

### Thermal Shock Properties

[The results of tests to compare the ability of the various refractory materials to withstand thermal shock are summarized in figure 7] and photographs → 6 showing the condition of various materials after the tests are presented in



figures 8 to 13. As can be seen, the materials varied greatly in their ability to withstand severe thermal shock without cracking and it is important to note that the variation was as great between the various zirconia products as between the different types of materials.

Zirconia.- Figures 8 to 10 show visually the difference between the various zirconia products tested and illustrate the wide variety of shock damage observed. As can be seen, [the partially calcia-stabilized material] (zirconia A) exhibited the best thermal shock capability of any of the zirconia materials tested and zirconia B, a fully calcia-stabilized material, proved superior to the available zirconia products [materials C and E, figs. 8 and 10] [utilizing yttria and ceria stabilization.] (See table I.) It should be also noted, however, that a wide difference in properties was found when comparing various calcia-stabilized zirconia products. (Compare materials A, B, and D of fig. 9.)

[On the basis of these tests, it must be concluded that the calcia-stabilized zirconia materials have the best thermal-shock resistance and, as would be expected from the literature] (refs. 4 and 5), [the best shock resistance is obtained in a partially stabilized zirconia. Other factors such as impurities, grain size, product density, and processing are known to influence final material performance; therefore, it appears that an actual test remains the only way to make final comparisons of the available products.] As demonstrated by the results of repeated cycling of the better zirconia of this test series (zirconia A and B in fig. 11), the partially calcia-stabilized material (zirconia A) is capable of repeated cycling without severe breakdown and is considered the best type of current zirconia material for use as brickwork and pebbles in the high-temperature regions of a 4000° F heat exchanger.

Magnesia.- The results of comparison tests between magnesia refractory brick and the best zirconia product of this test series (zirconia A) are shown in figure 12. As can be seen, the [magnesia exhibited marked cracking tendencies at three heating cycles. Distinct signs of material vaporization on the high-temperature face of the brick were noted. This vaporization was expected from the literature] (ref. 6) [since this material is reported to exhibit high vapor pressure. The test results would not completely rule out consideration of magnesia as a possible material for heat-exchanger use; however, zirconia A appears to be superior in most respects for usage between 3500° F to 4000° F.]

Thoria.- [The refractory thoria was compared with zirconia A at the normal zirconia operating range (3000° F to 4000° F) although thoria was being considered as a possible material for increasing the range of heat-exchanger operation to temperatures well above 4000° F. Thermal-shock results] (fig. 13) [showed that the bricks spalled very severely when compared with zirconia A. On the basis of these tests, thoria is not considered to be acceptable for heat-exchanger use even in the 4000° F range. It should also be noted that the radioactive nature of thoria would complicate all operations and maintenance procedures on a facility using this material.] →<sup>9</sup>



## High-Temperature Static Load Capability

Zirconia.-- Results of tests to define the maximum load capability in the 3500° F to 4000° F temperature range for the several zirconia products evaluated are presented in figures 14 and 15. These results show that the products ranked most acceptable for thermal-shock properties (zirconia A, B, and C) all lost strength rapidly (fig. 15) at the elevated temperatures and test results (figs. 14(b), 14(c), and 14(d)) indicate that loads above 4 pounds per square inch will produce compressive failures in any of these materials at temperatures above 4000° F. For zirconia products D and E, load capability was higher and the 1-inch cubes of these materials withstood loads of 6 pounds per square inch at 4000+° F without fracture (figs. 14(e) and 14(f)). The poor thermal-shock capacity of these two materials (discussed in the previous section) prevented the exact evaluation of maximum load capabilities, since the loading weights made from these materials spalled severely from thermal shock as shown in figure 14(f). These results primarily serve to indicate again the wide range of properties found in zirconia products of different compositions.

The most significant result of the loads testing is shown in figure 15 where it can be seen that the fully calcia-stabilized zirconia product B had appreciably lower load capability than the partly calcia-stabilized zirconia A. This difference is most pronounced at the moderate temperatures (3000° F to 3800° F); thus, heater components such as pebbles made from the fully stabilized material would be more prone to compacting in the hot sections of the heat exchanger than would pebbles made from the partly stabilized product.

Magnesia and thoria.-- The high-temperature load capability of these materials could not be accurately defined because of reactions between these materials and the zirconia floor of the test kiln. Generally, both refractory materials exhibited good compressive strength properties, and the thoria material withstood loads as high as 8 pounds per square inch at 4200° F.

## Evaluation of Crystal Stability

The effect of repeated thermal cycling between 1100° F and 2100° F on the cold strength for the various zirconia materials is presented in figure 16. There is a wide variation in strength between the various zirconia products, but especially evident is the severe loss in strength shown for the partially calcia-stabilized zirconia A. These data as well as data from tests of pebbles (fig. 17) illustrate the need to consider this property of zirconia for cases where the material may be subjected to cycling at the lower temperature levels. Although these results confirm general concepts that fully calcia-stabilized and rare-earth-stabilized zirconia products will not suffer severe inversion breakdown, it must be remembered that the stabilization process for zirconia is not fully understood to date and it appears that product testing may be required for some time to insure attainment of the product properties desired in the particular zones of heater installations.

## Contact Reactions Between Refractories

The results of tests made to define the limiting temperature for interface contact between the various refractories and summarized in figure 18 and photographs showing typical reaction damage for some of the materials are shown in figures 19 to 22. As was expected from the literature (ref. 7), zirconia was found to react with alumina and magnesia rather severely for temperatures above approximately  $3100^{\circ}\text{F}$  (fig. 18), and furthermore an unexpected reaction between zirconia and thoria was encountered when these materials were in contact under load at temperatures exceeding  $3500^{\circ}\text{F}$ . Typical examples of the interface reaction damage between zirconia and magnesia or thoria are shown in figures 19 to 21. As can be seen, the reacting surfaces weaken as the materials react at the interface and migrate into each other until finally a significant failure results (fig. 21(b)) at the interface. From these results it is apparent that extreme caution must be exercised in attempting to place other refractory materials in contact with zirconia in heat-exchanger usage.

In considering the other possible refractory combinations, it is seen (fig. 18) that no reaction was noted between thoria and magnesia to the limiting temperature of this test ( $4000^{\circ}\text{F}$ ), and for the case of thoria and alumina only mild reaction was noted at temperatures approaching normal maximum use temperatures for the alumina. Combinations of magnesia and alumina are known to be compatible up to normal use temperatures for alumina (approximately  $3400^{\circ}\text{F}$ ). (See ref. 8.)

## Refractory Choice in Heat-Exchanger Design

As was indicated earlier in this paper, heat-exchanger usage subjects refractories to a wide variation in operation environments and, as a result, the important properties required in a material vary from point to point in a heater. When this variable environment is considered in the light of the test results for the refractory materials considered herein, it is seen that no one material appears to be optimum for usage at all points in the system. The choice of materials for the system then becomes a compromise based on the most important factors at each region and the materials currently considered the best choices for use in a  $3200^{\circ}\text{F}$  to  $4000^{\circ}\text{F}$  heat exchanger are as follows:

High-temperature zone.- For the inner liner brick and top layers of pebbles in the upper high-temperature sections (approximately  $3000^{\circ}\text{F}$  to  $4000^{\circ}\text{F}$ ) of the heat exchanger where materials are subjected to burner flame temperatures of  $4500^{\circ}\text{F}$  or more during heating cycles, thermal-shock capability is of prime importance with hot load capacity also significant. Here a partially calcia-stabilized zirconia, such as zirconia A, must be considered as the best material since the fully stabilized types of zirconia, the thoria, and the magnesia refractories all had poor thermal-shock capabilities compared with the best zirconia materials. It is also pointed out that none of the other refractories can be mixed by intent or accident with zirconia in this region or low-temperature reactions will result in refractory failure.

Moderate-temperature zones.- For the moderate-temperature sections of the system ( $1500^{\circ}\text{F}$  to  $3000^{\circ}\text{F}$ ) such as the middle depths of the pebble bed, the

middle sections of the liner, and the insulating brickwork at upper levels, the fully calcia-stabilized type zirconia appears to be the most acceptable material for use. In this region only moderate thermal-shock properties are required; however, high resistance to inversion-type strength loss is needed since the critical inversion temperatures of 1800° F to 2100° F for zirconia will be repeatedly reached somewhere in this zone. The fully calcia-stabilized zirconia has been successfully used in this region in the Langley 11-inch ceramic heated tunnel and is presently considered the best material choice for this middle temperature zone. Although the temperature range is sufficiently low to suggest use of other low-temperature refractories, this approach must be used with great caution to avoid incurring reaction damage (contamination) in the higher temperature zones of the zirconia by particle transport during facility blowdown.

Low-temperature zones.- Only very tightly bonded materials such as alumina are considered acceptable for mixed usage even in the lower temperature sections such as the lower liner and pebble bed since airflow would transport loose particles to the hot zones above. It should also be noted that extreme care must be exercised in using other materials for insulation within the walls of heat exchangers as air channeling (bypassing through walls) can transport these materials unless the system is properly designed. The acceptability of high-purity, high-density alumina for such usage is considered to be well established, as this material has been continuously used in the lower sections of the subject heat exchanger (fig. 1) without causing contamination of the zirconia materials.

On the basis of tests reported here and the experience gained in operating the subject heat exchanger, it can be said that available materials enable the construction and successful operation of air heat exchangers to temperatures of approximately 4100° F. It should be pointed out, however, that the best current material (calcia-stabilized zirconia) can only be graded as just acceptable since appreciable yearly maintenance is required and airstream contamination by loose grains of zirconia can be a severe problem unless flow velocity through the pebble bed is kept very low by initial design.

### CONCLUSIONS

Studies of the comparative properties of several high-temperature refractory oxide materials available for use in wind-tunnel heat exchangers leads to the following conclusions:

1. Fused-grain partially calcia-stabilized zirconia has the best thermal-shock resistance of all the materials tested and is the most acceptable material for use in the high-temperature sections of heat exchangers for operation above 3400° F.

2. In general, all calcia-stabilized zirconia product exhibited thermal-shock properties superior to the experimental rare earth (ceria and yttria) stabilized materials available for study.

3. Thoria and magnesia both appear unsuitable for cyclic use at high temperatures because of poor thermal-shock capabilities.

4. Stabilized zirconia undergoes a rapid loss of static load capability above 3000° F and test results indicate loadings should not exceed approximately 4 to 6 pounds per square inch in high-temperature sections of a zirconia heat exchanger.

5. Deterioration (strength loss) due to crystalline inversion with zirconia products varies with degree of stabilization. In general, fully stabilized products using either calcia or rare earth materials for stabilization suffer little strength loss on cycling; however, the partially stabilized materials may lose all strength and crumble after as few as 50 cycles in the critical temperature range (approximately 1600° F to 2100° F).

6. Studies of the <sup>ca</sup>reaction temperature for the various refractories indicate that zirconia reacts (forms solid solution on contact) with all other materials tested at temperatures appreciably lower than the normal use temperatures of the individual materials.

7. The variation in thermal shock and stability properties of zirconia products available requires careful evaluation of products considered for heat-exchanger use. *end*

Langley Research Center,  
National Aeronautics and Space Administration,  
Langley Station, Hampton, Va., June 22, 1964.

## REFERENCES

1. Trout, Otto F.: Design, Operation, and Testing Capabilities of the Langley 11-Inch Ceramic-Heated Tunnel. NASA TN D-1598, 1963.
2. Buckley, John D.: Deterioration of Calcia-Stabilized Zirconia. NASA TN D-1595, 1962.
3. Anon.: Ceramic Data Book, 1961-1962. Cahners Pub. Co., Inc. (Chicago, Ill.), c.1961, pp. 428-429.
4. Curtis, C. E.: Development of Zirconia Resistant to Thermal Shock. Jour. American Ceramic Soc., vol. 30, no. 6, June 1947, pp. 180-196.
5. Whittemore, O. J., Jr., and Marshall, D. W.: Fused Stabilized Zirconia and Refractories. Jour. American Ceramic Soc., vol. 35, no. 4, Apr. 1952, pp. 85-89.
6. Norton, F. H.: Refractories. Third ed., McGraw-Hill Book Co., Inc., 1949.
7. Anon.: Stabilized Zirconia. Customer Bulletin CP8.5.1, Refractories Div., Norton Co. (Worcester, Mass.), April 7, 1958.
8. Campbell, I. E., ed.: High-Temperature Technology. John Wiley & Sons, Inc., c.1956.

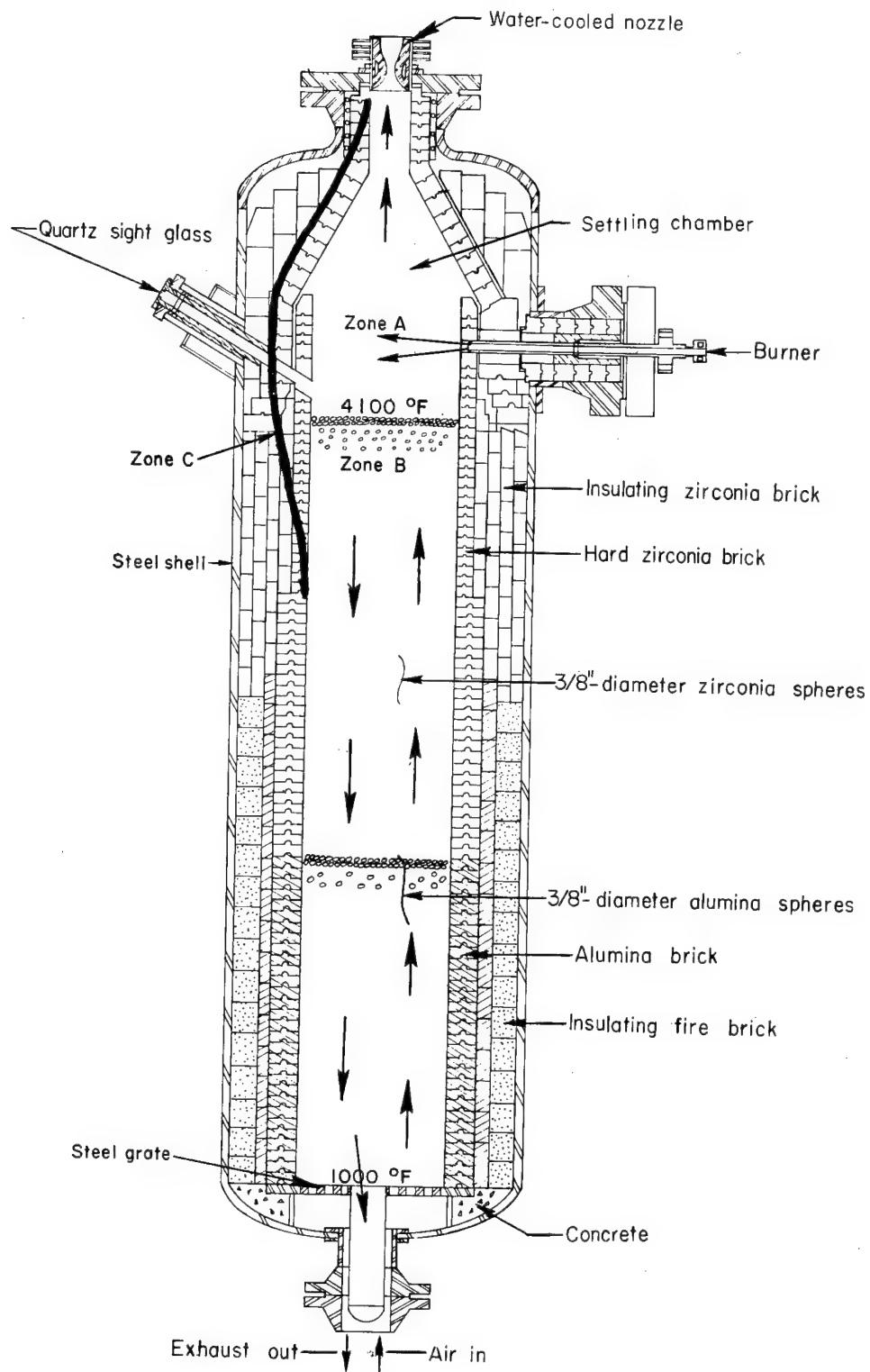
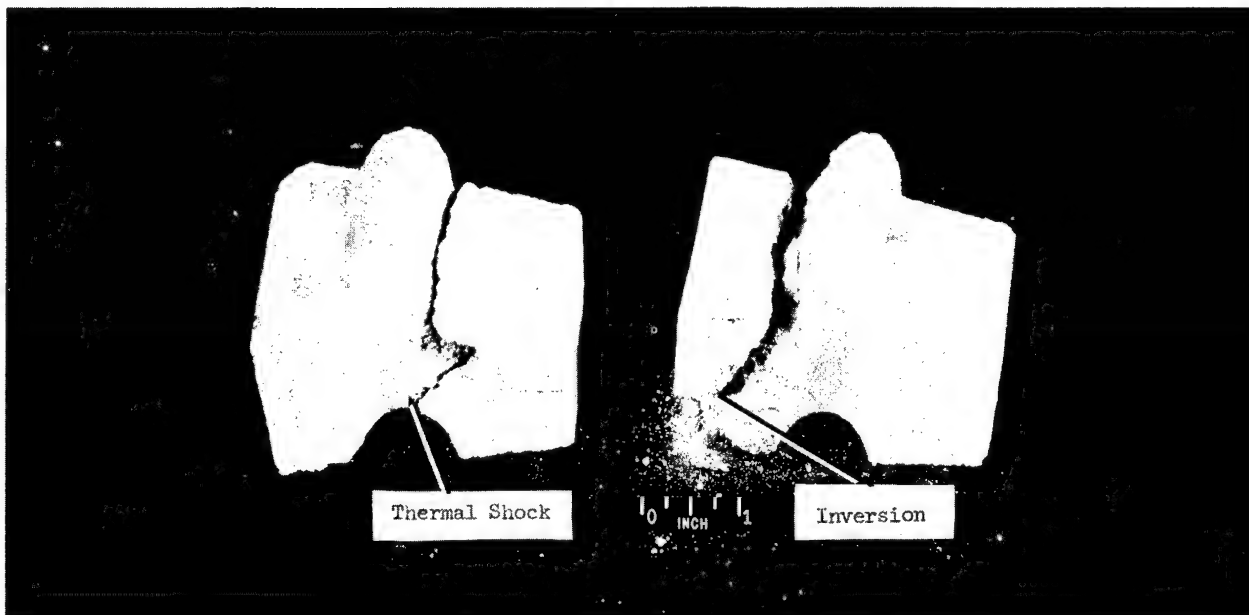


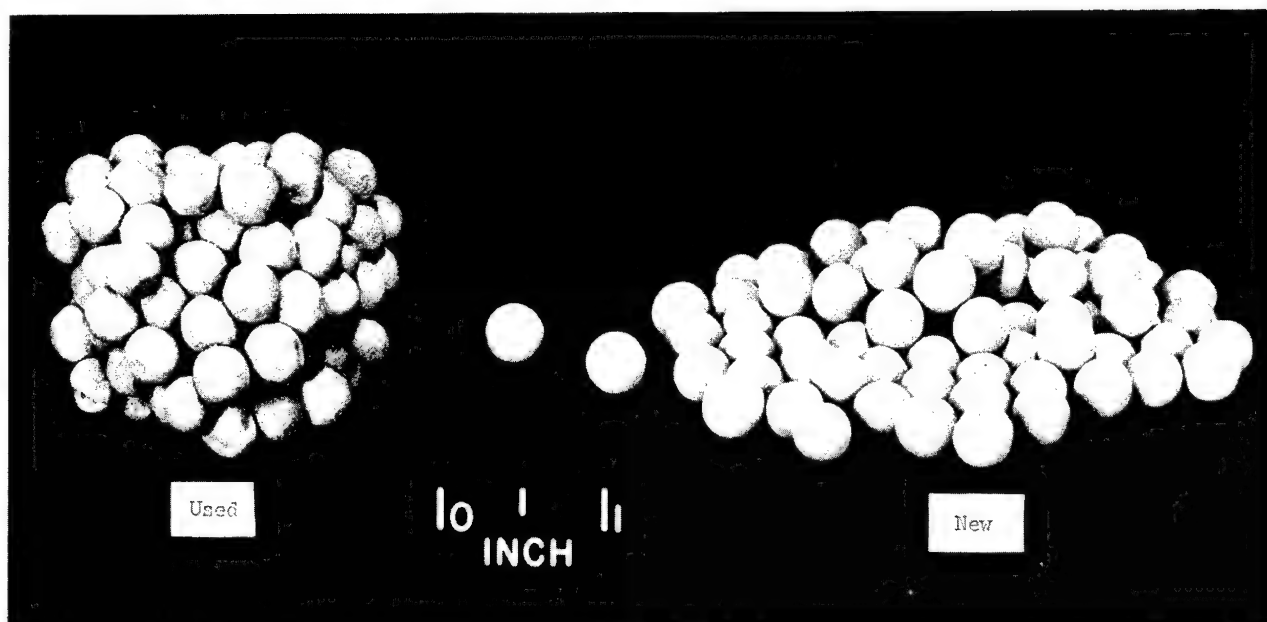
Figure 1.- Section view of ceramic heat exchanger.





(a) Thermal shock and inversion damage.

L-59-7449.1



(b) Pebble compacting from load at temperature.

L-64-4400.1

Figure 2.- Typical brick and pebble damage observed with standard calcia-stabilized zirconia.  
Zirconia A.

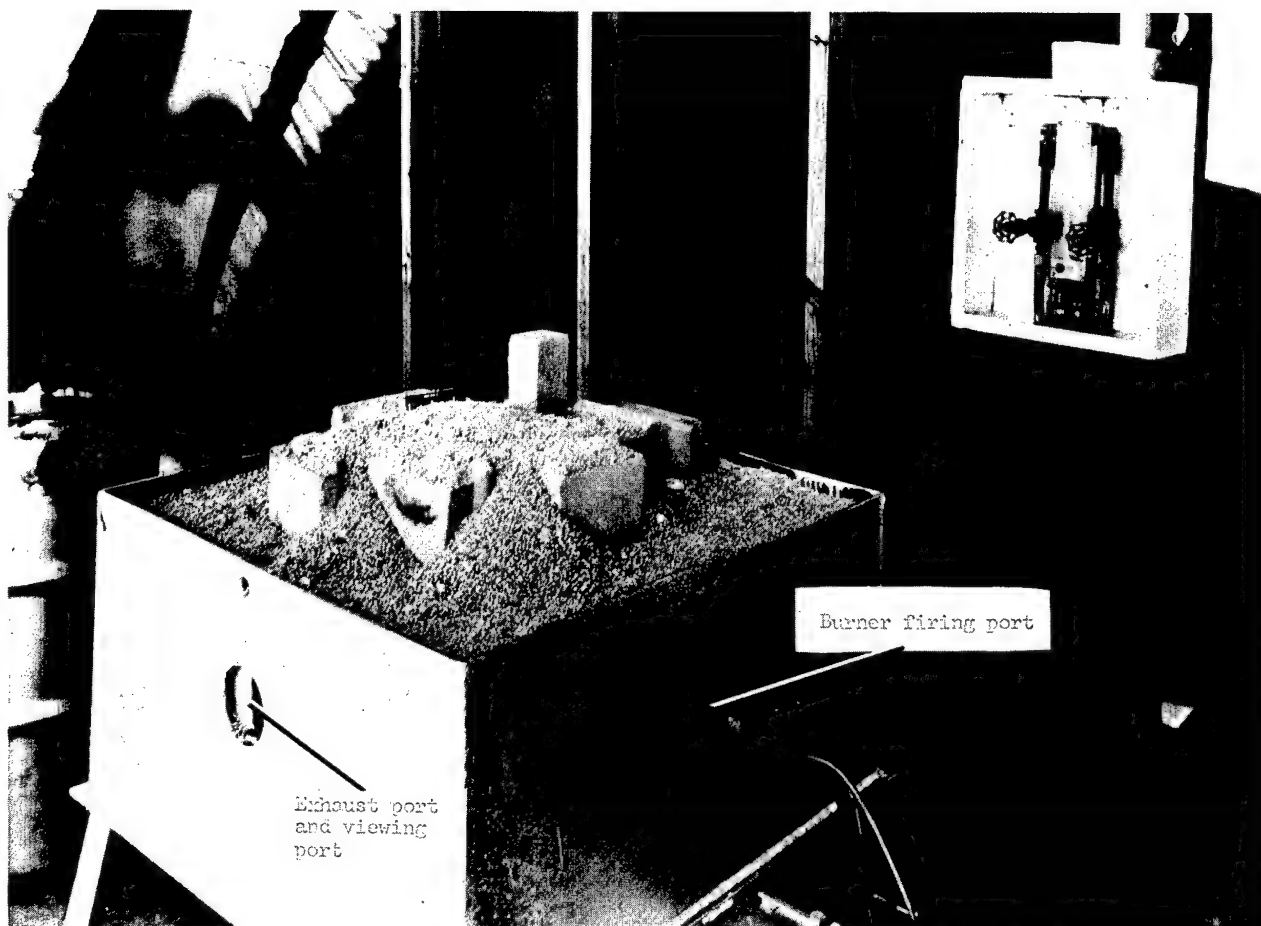
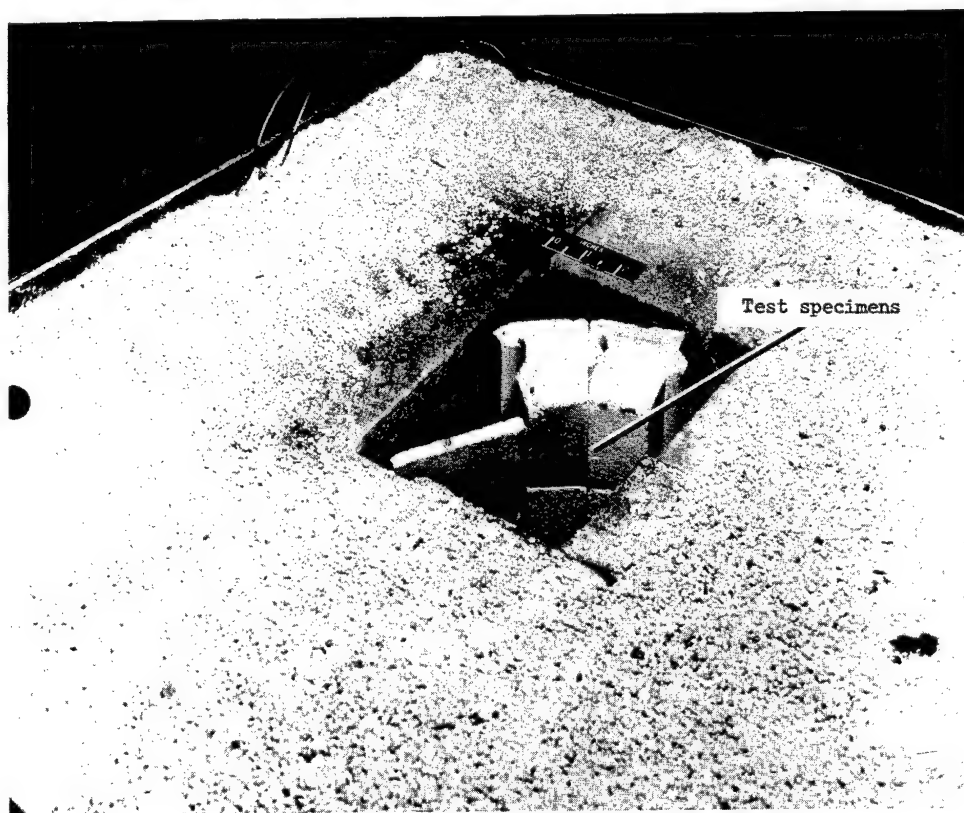
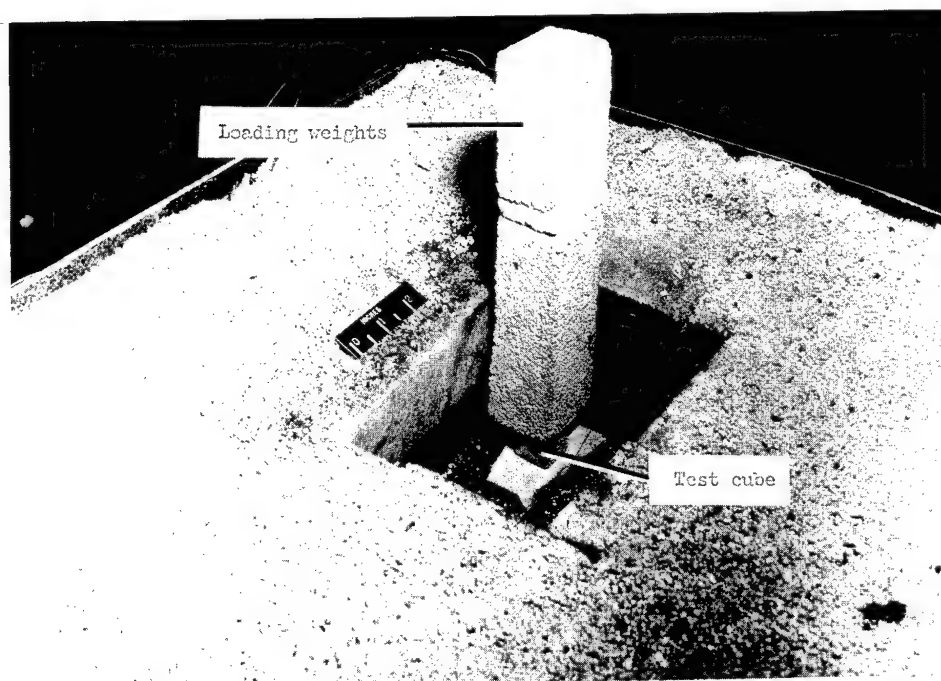


Figure 3.- Typical kiln setup ready for firing with test cube under load. L-62-3355.1



L-62-3359.1

Figure 4.- Arrangement of test bricks in kiln for thermal-shock tests.



L-62-3356.1

Figure 5.- Arrangement of test cube in kiln for hot load tests.

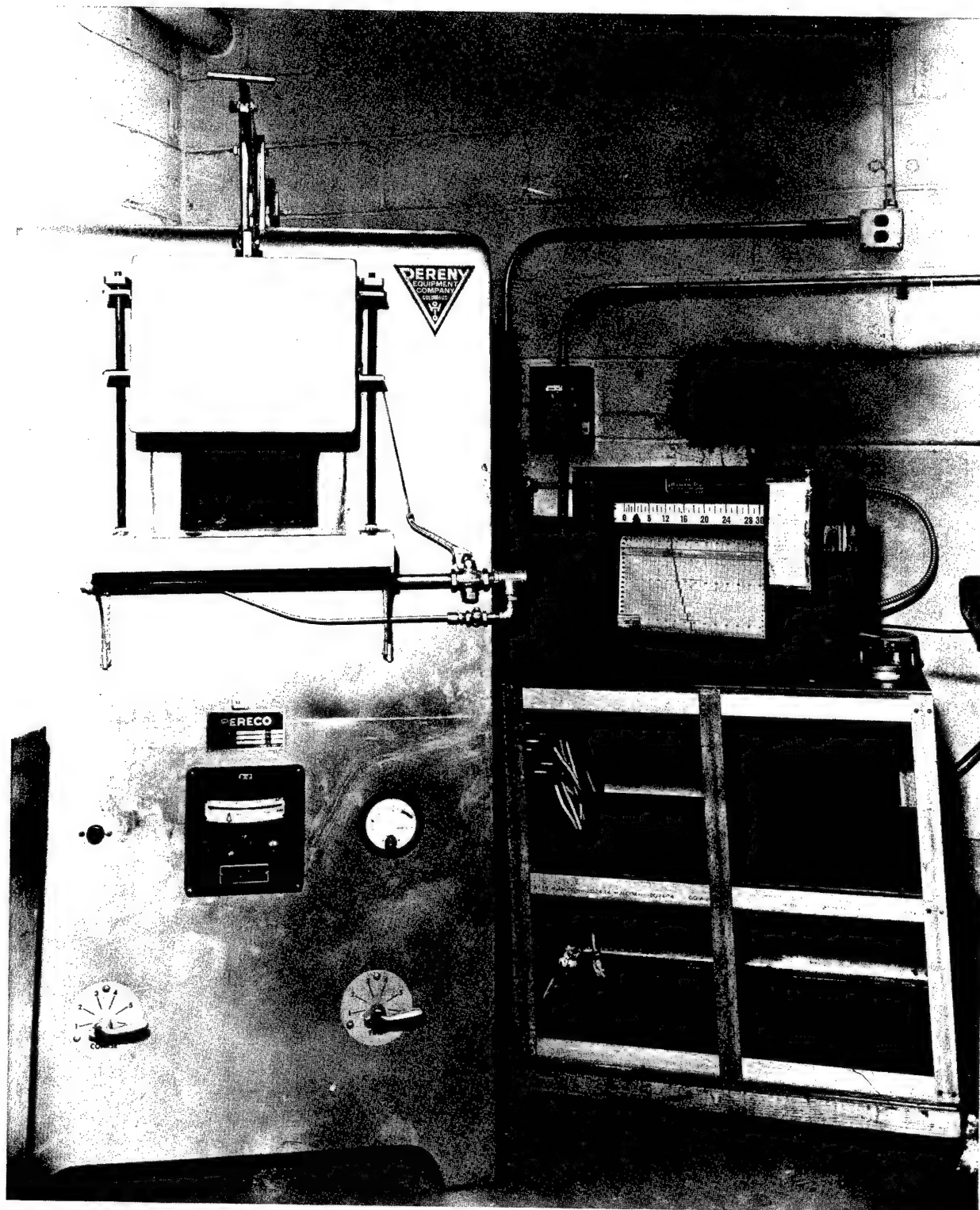


Figure 6.- Electric furnace setup with Brown recorder for thermal cycling tests. L-62-3358

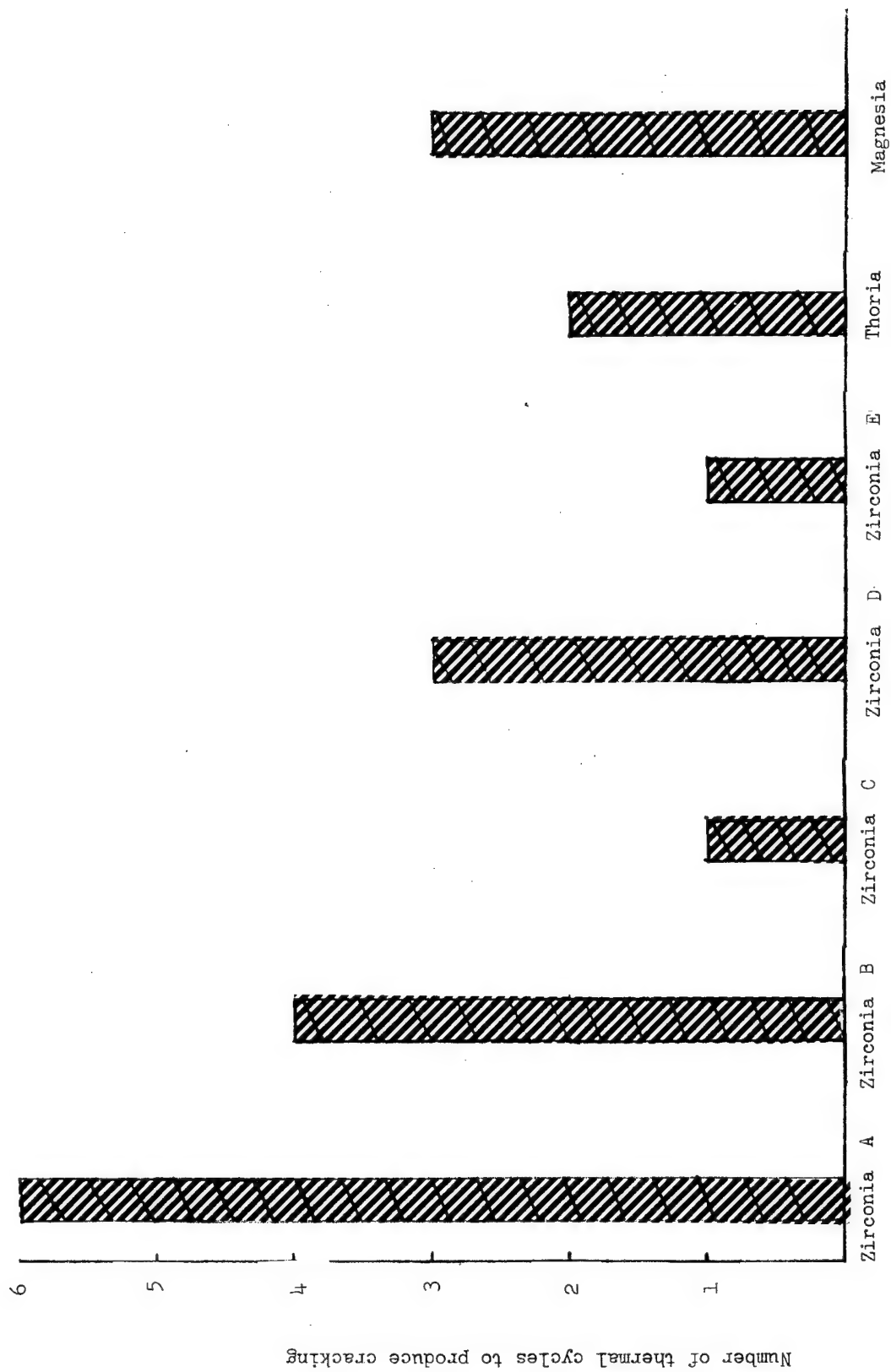
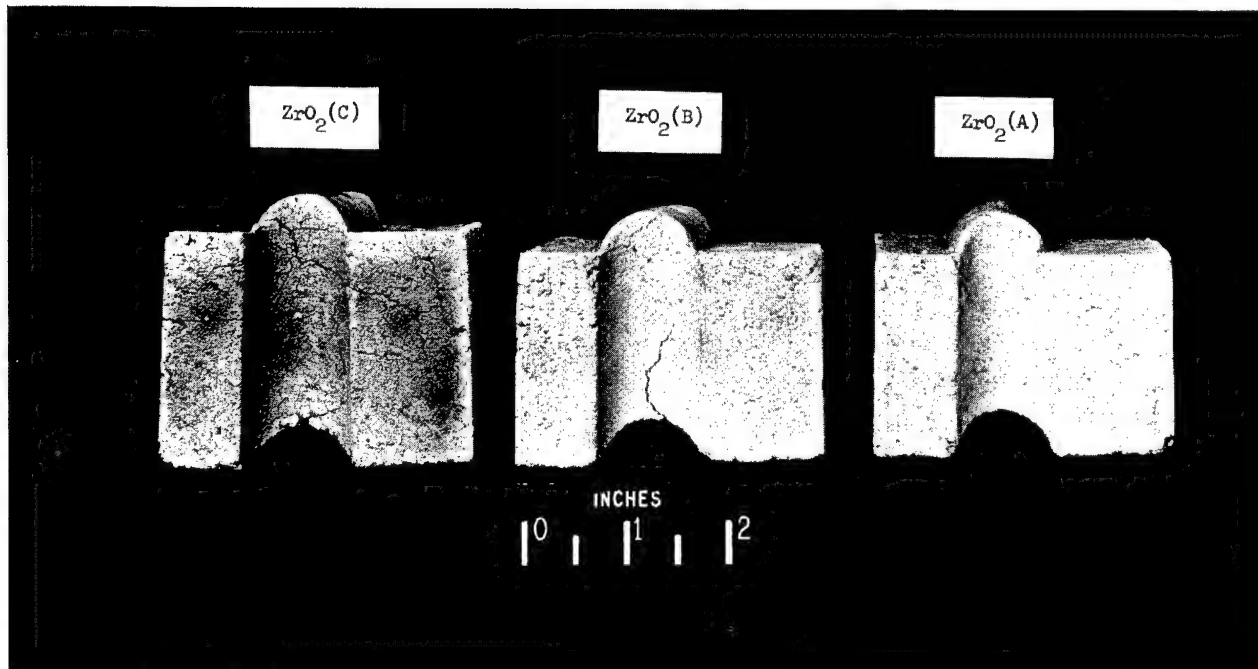
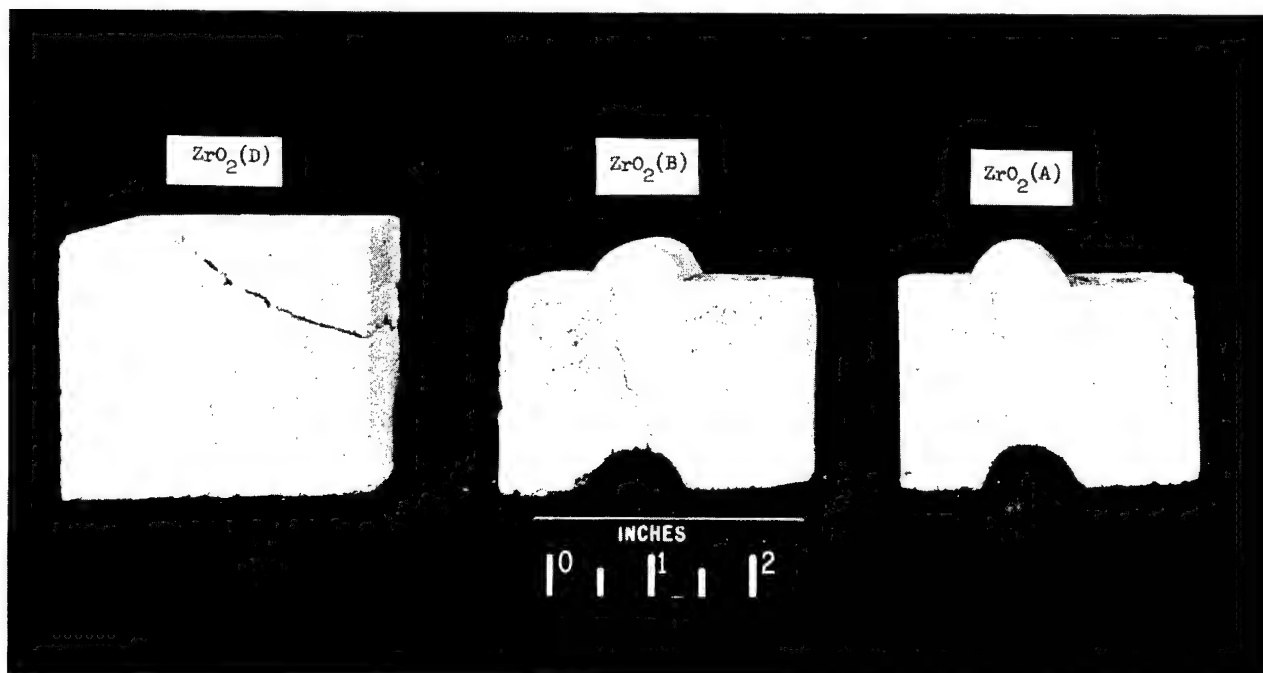


Figure 7.- Number of thermal cycles required to produce cracks in refractory bricks. Ambient to 4000° F and then cycled from 3000° F to 4000° F.



L-62-4470.1

Figure 8.- Comparison of effect of thermal shock on zirconia A, zirconia B, and zirconia C after 2 cycles between 80° F and 4000° F and 2 cycles between 3000° F and 4000° F.



L-62-4467.1

Figure 9.- Comparison of effect of thermal shock on zirconia A, zirconia B, and zirconia D after 1 cycle between 80° F and 4000° F and 3 cycles between 3000° F and 4000° F.



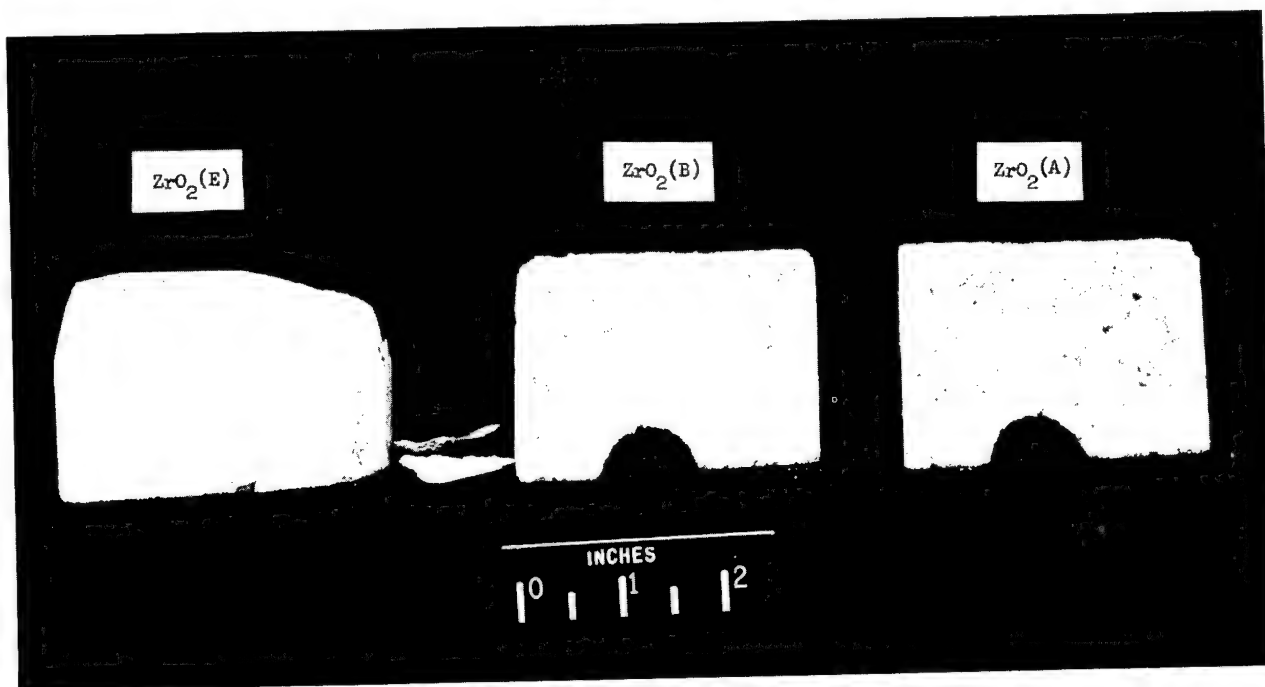


Figure 10.- Comparison of effect of thermal shock on zirconia A, zirconia B, and zirconia E after 1 cycle between 80° F and 4000° F. L-62-4466.1

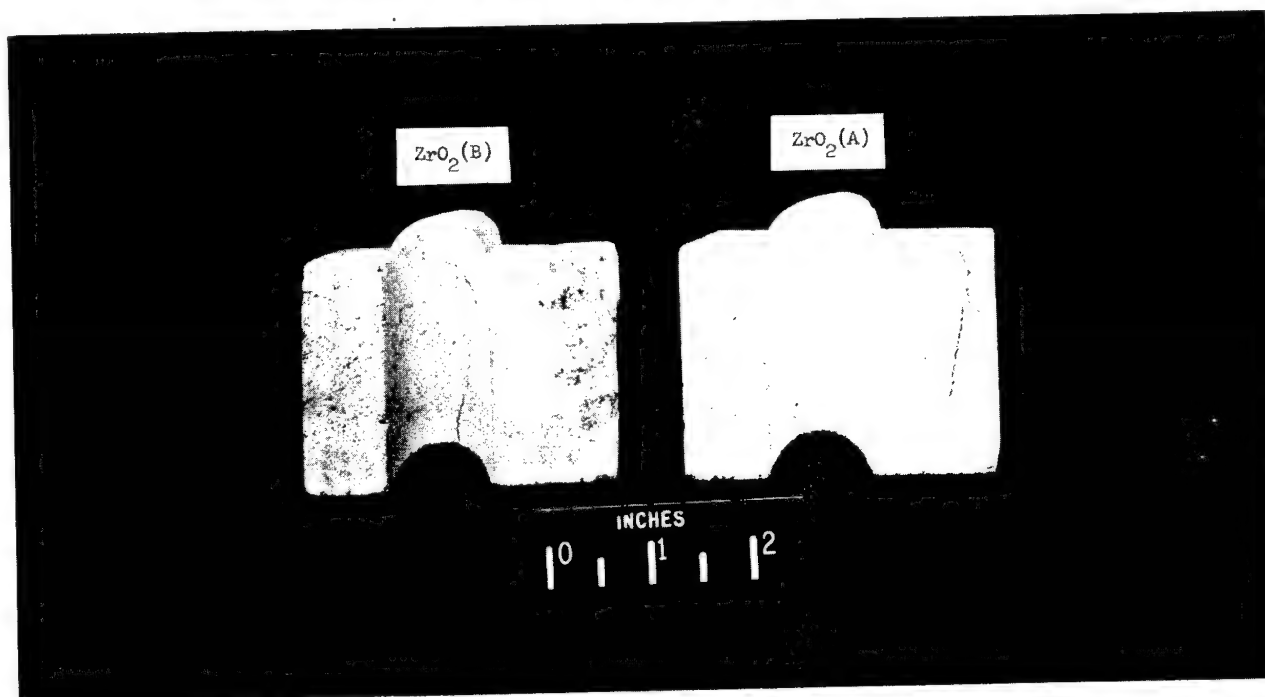


Figure 11.- Comparison of effect of thermal shock on zirconia A and zirconia B after 3 cycles between 80° F and 4000° F and 5 cycles between 3000° F and 4000° F. L-62-4468.1

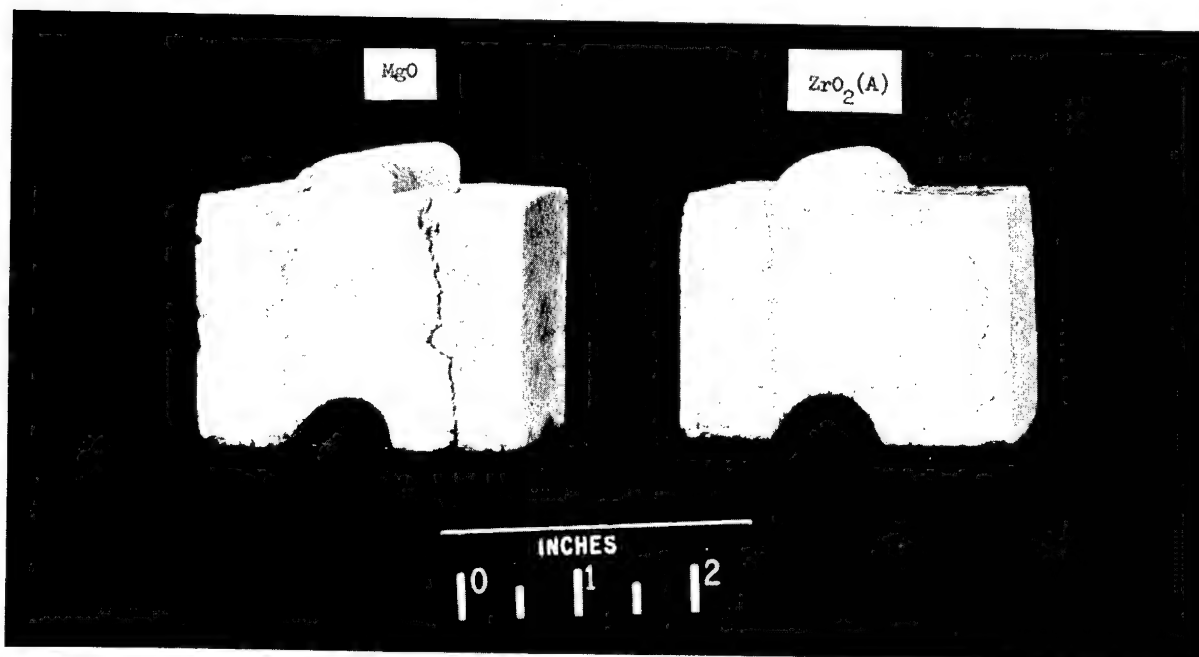


Figure 12.- Comparison of effects of thermal shock on magnesia and zirconia A after 2 cycles between 80° F and 3800° F and 1 cycle between 3000° F and 3800° F. L-62-4465.1

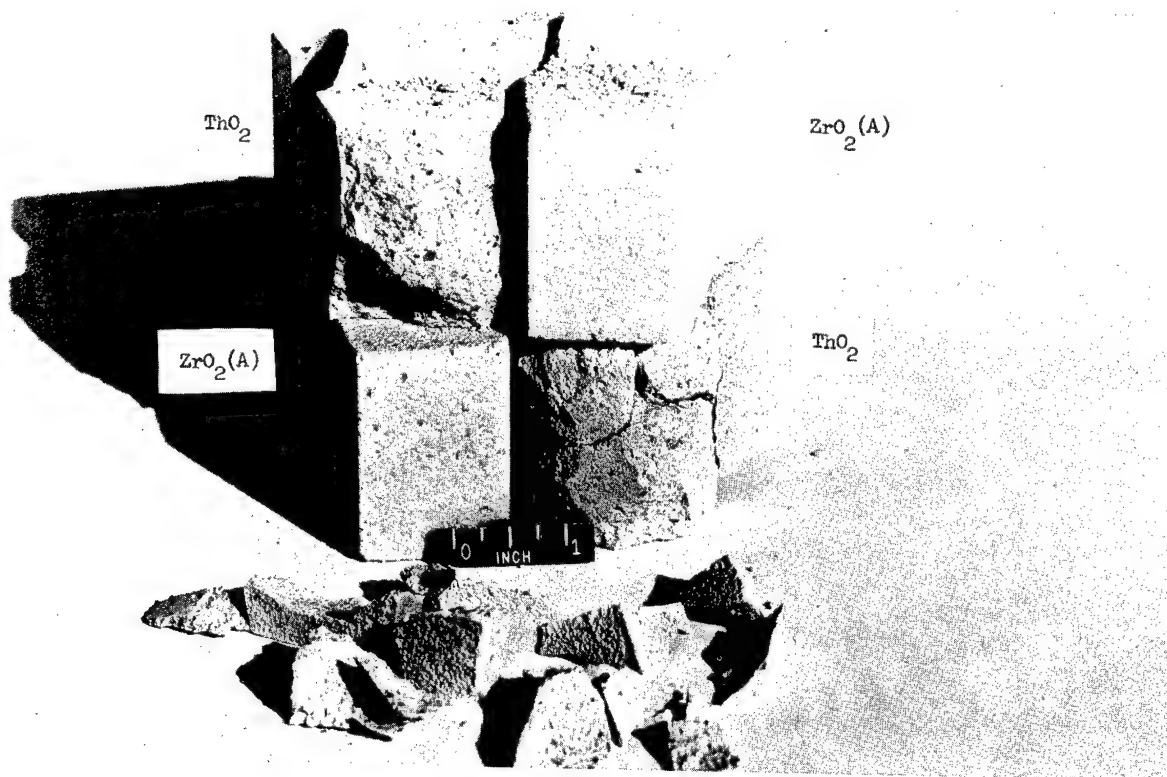
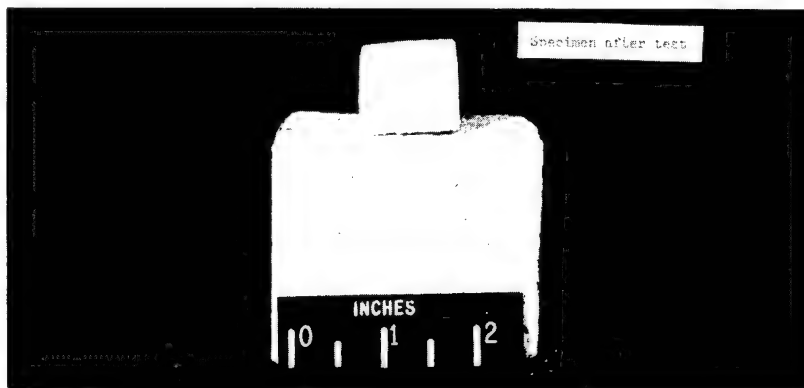
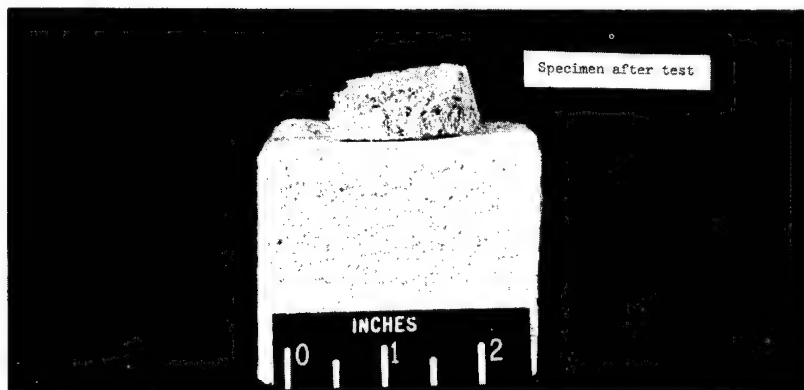


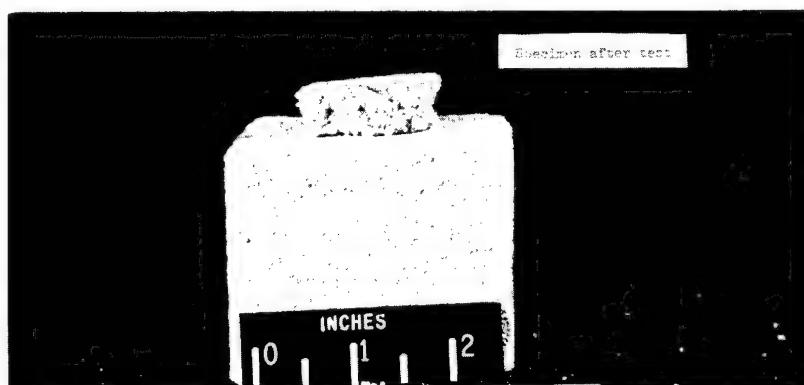
Figure 13.- Comparison of effect of thermal shock on thorium and zirconia A after 2 cycles from 80° F to 4200° F. L-59-6731.1



(a) Zirconia A; 4 pounds per square inch at 4100° F. L-62-4475.1

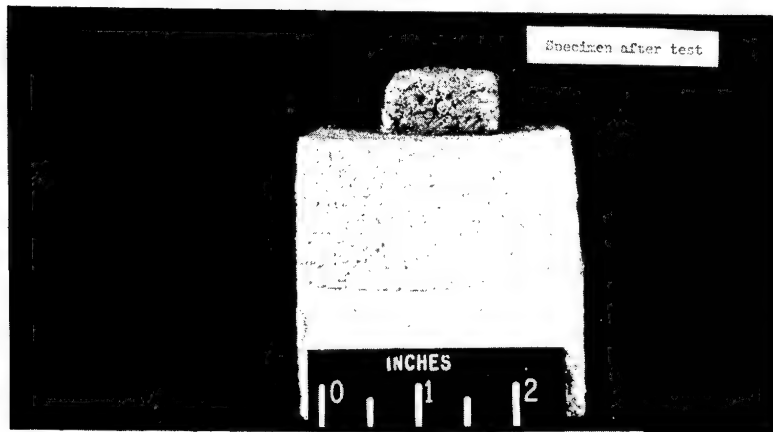


(b) Zirconia A; 6 pounds per square inch at 4100° F. L-62-4460.1

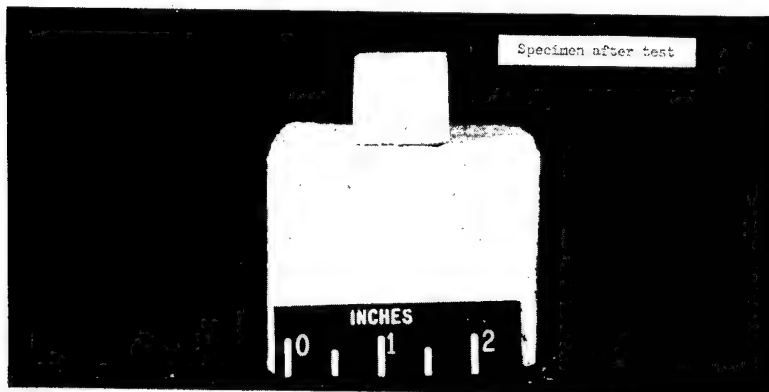


(c) Zirconia B; 4 pounds per square inch at 3650° F. L-62-4472.1

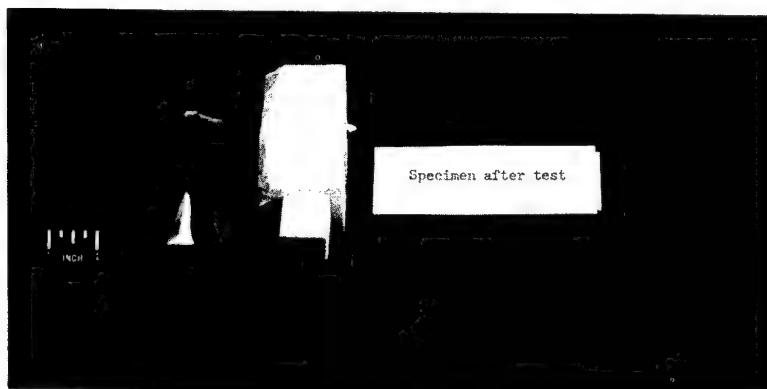
Figure 14.- Effect of load on zirconia cubes at elevated temperatures.



(d) Zirconia C; 4 pounds per square inch at 4100° F. L-62-4476.1



(e) Zirconia D; 6 pounds per square inch at 4000° F. L-62-4474.1



(f) Zirconia E; 6 pounds per square inch at 4050° F. L-61-1880.1

Figure 14.- Concluded.

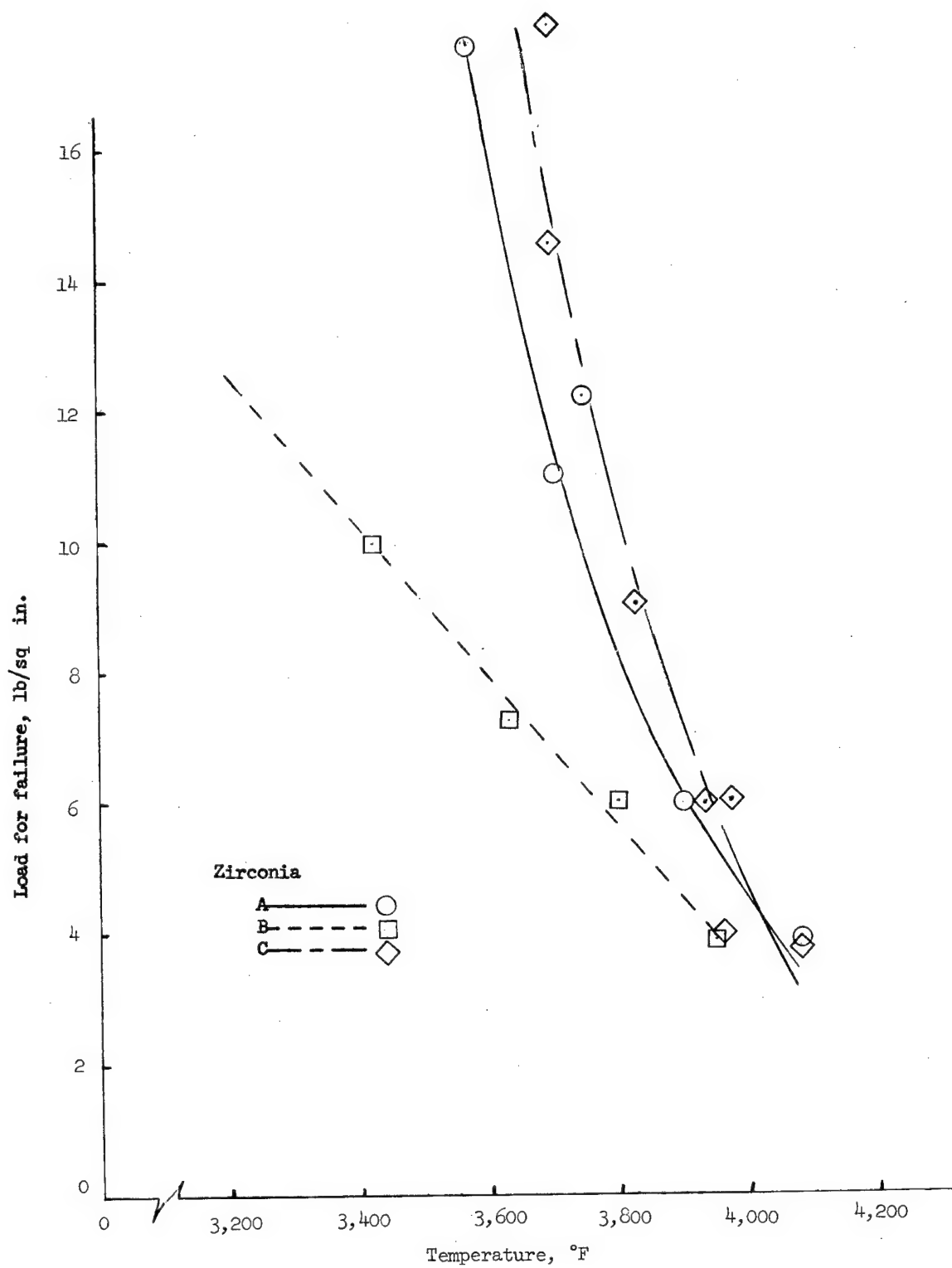


Figure 15.- Loads for compressive failure of 1-inch zirconia cubes.

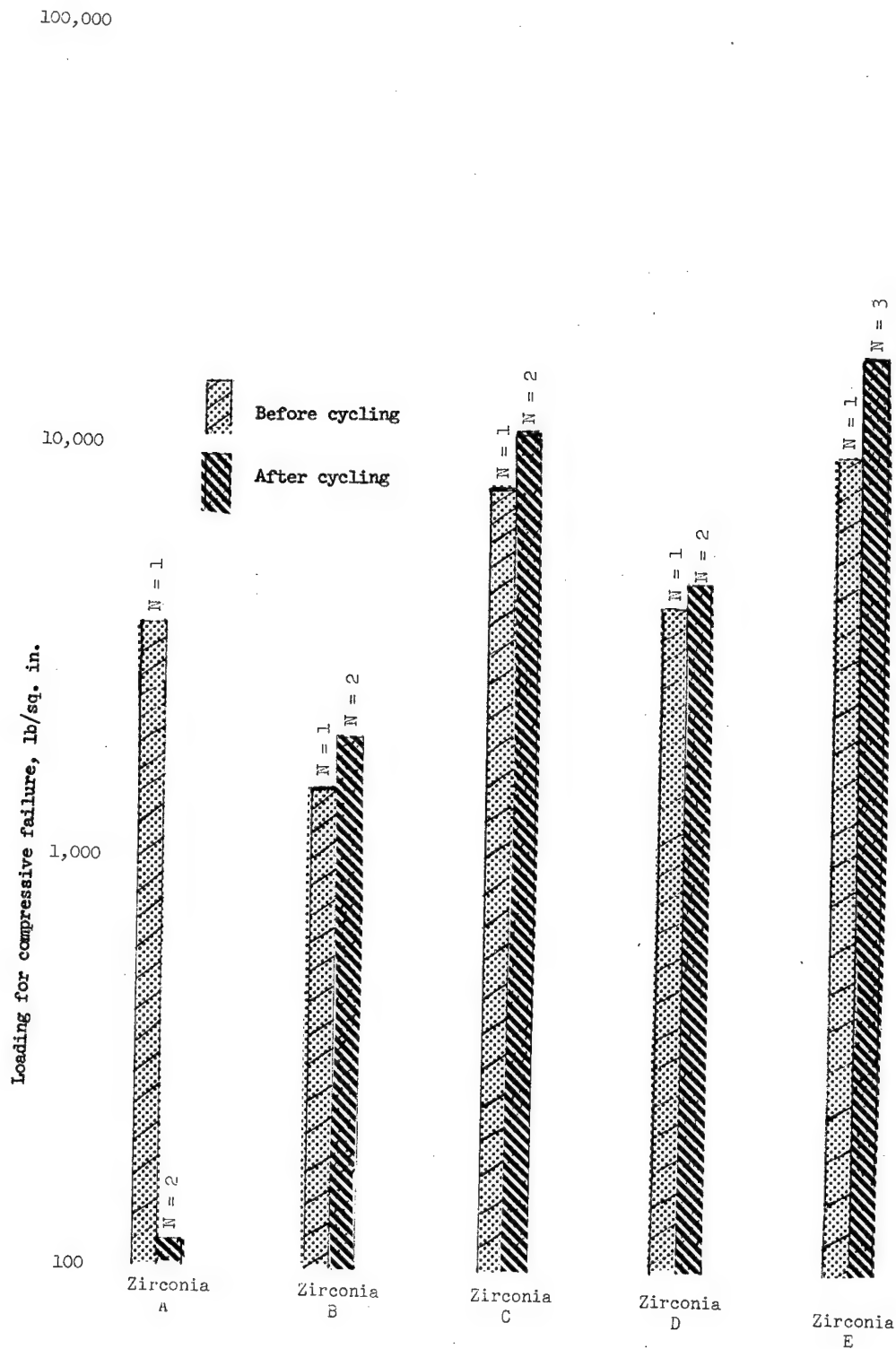


Figure 16.- Effect of thermal cycling in the inversion range on cold compressive strength of 1-inch zirconia cubes. Limited data samples indicated by N; 49 cycles from 1100° F to 2100° F.



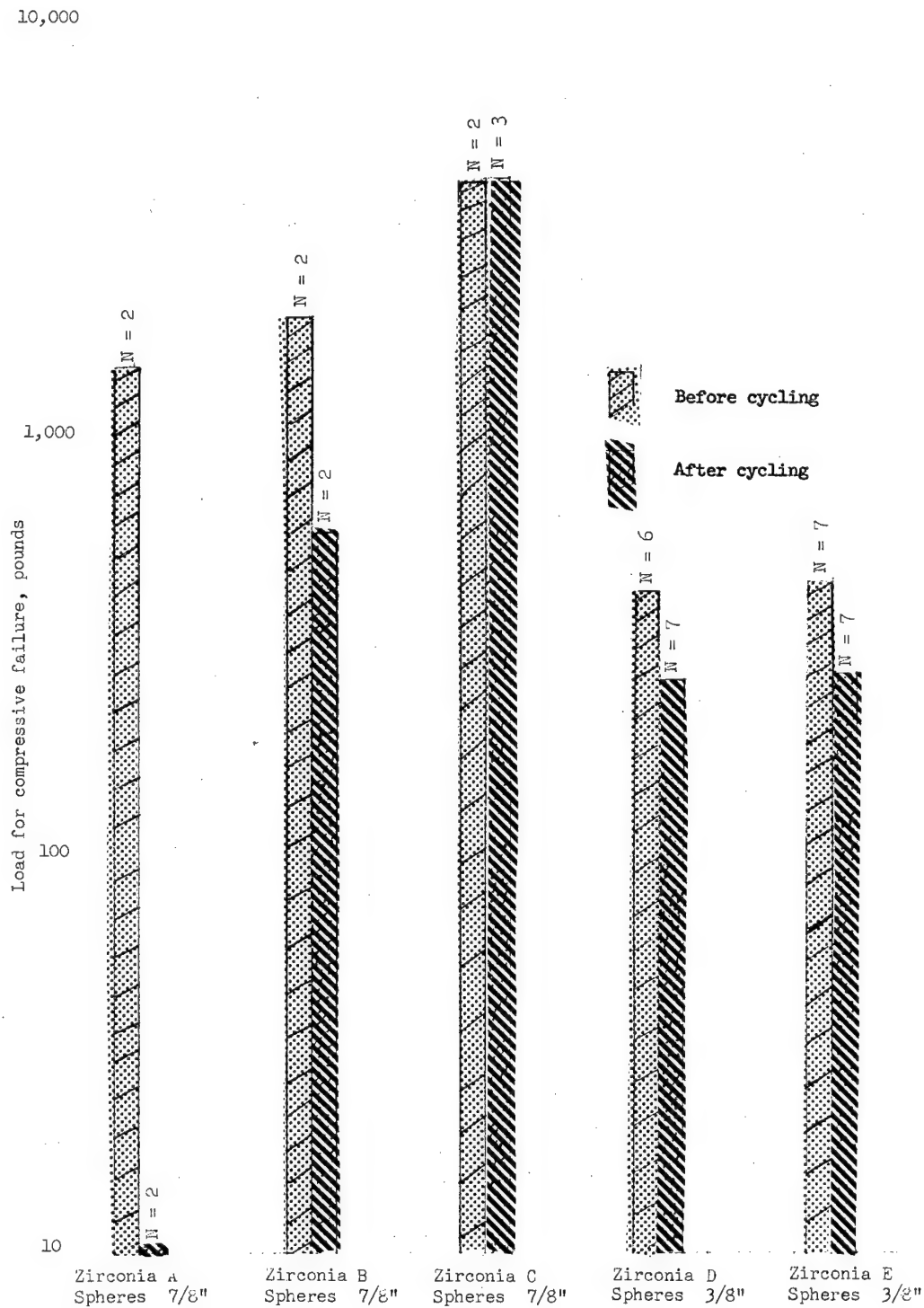


Figure 17.- Effect of thermal cycling in the inversion range on cold compressive strength of various zirconia refractories. Spheres; limited data samples indicated by N; 49 cycles from 1100° F to 2100° F.

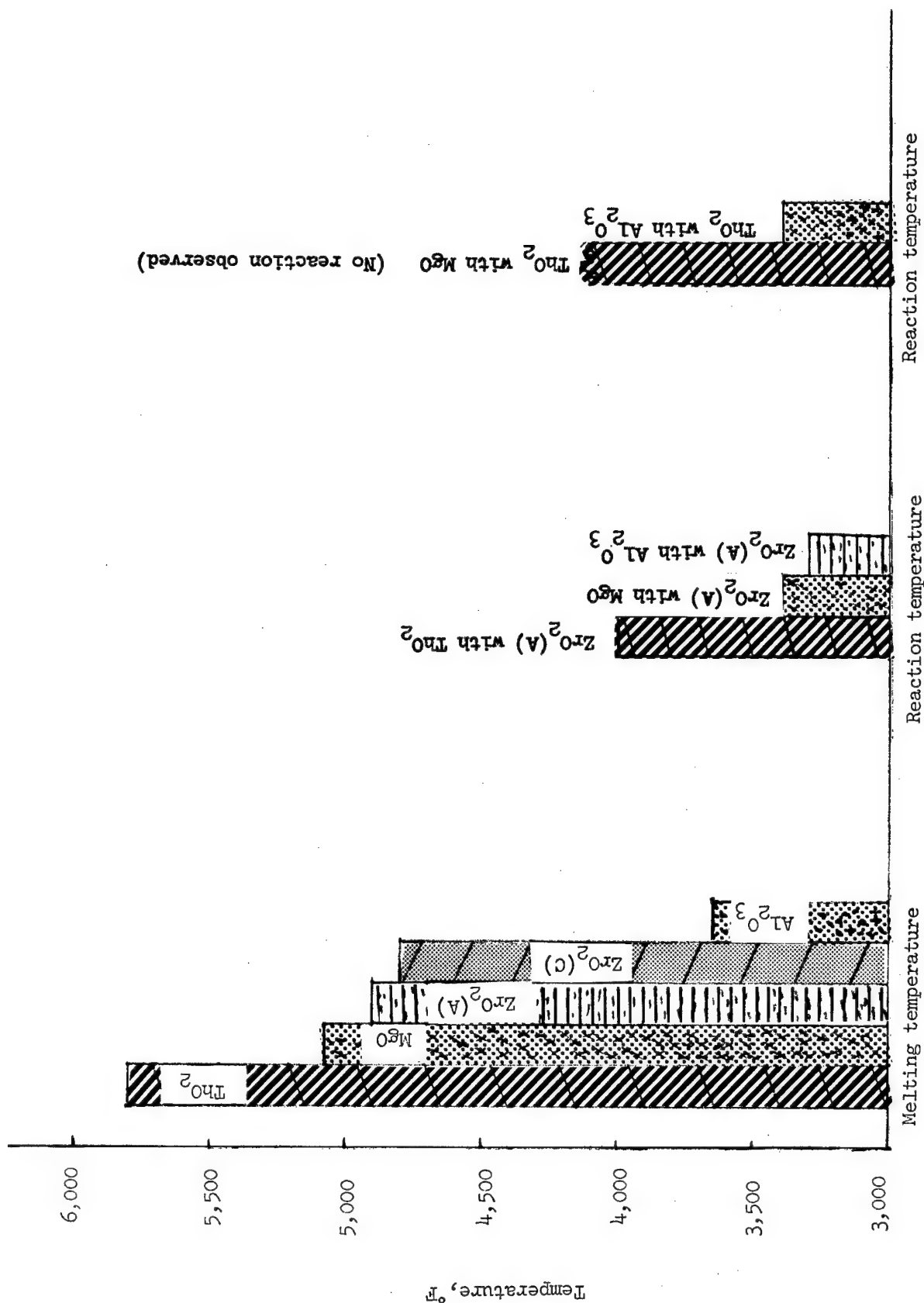
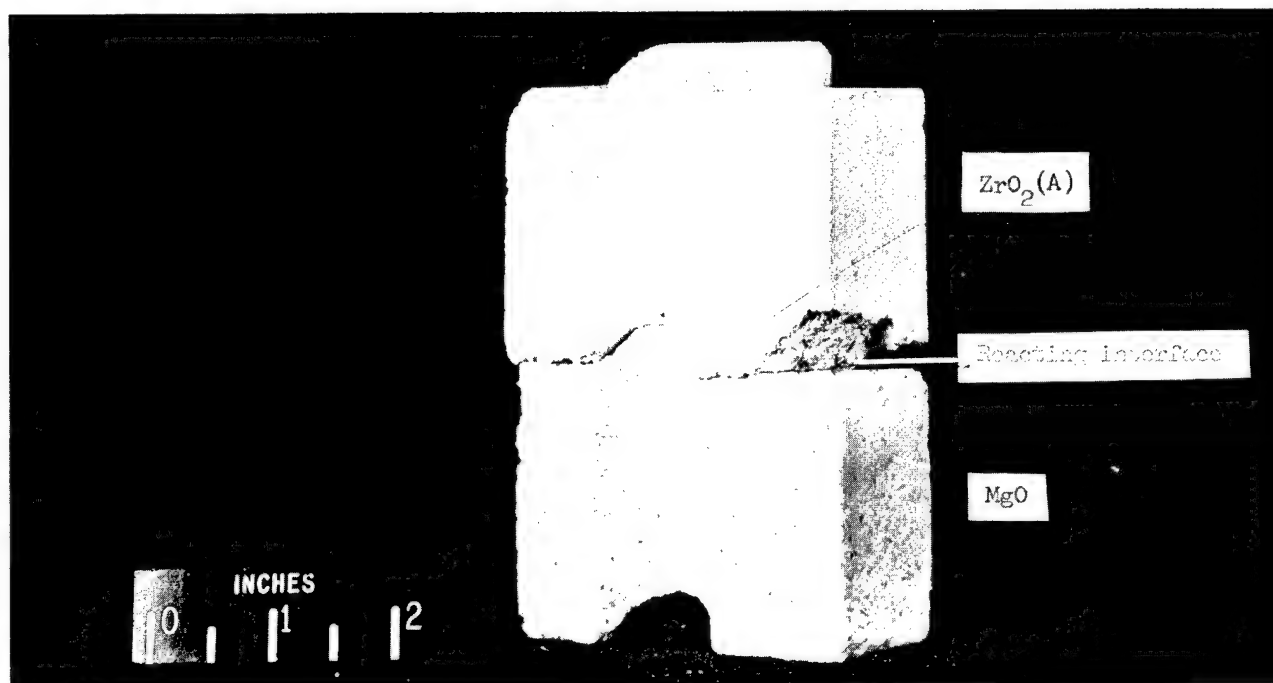
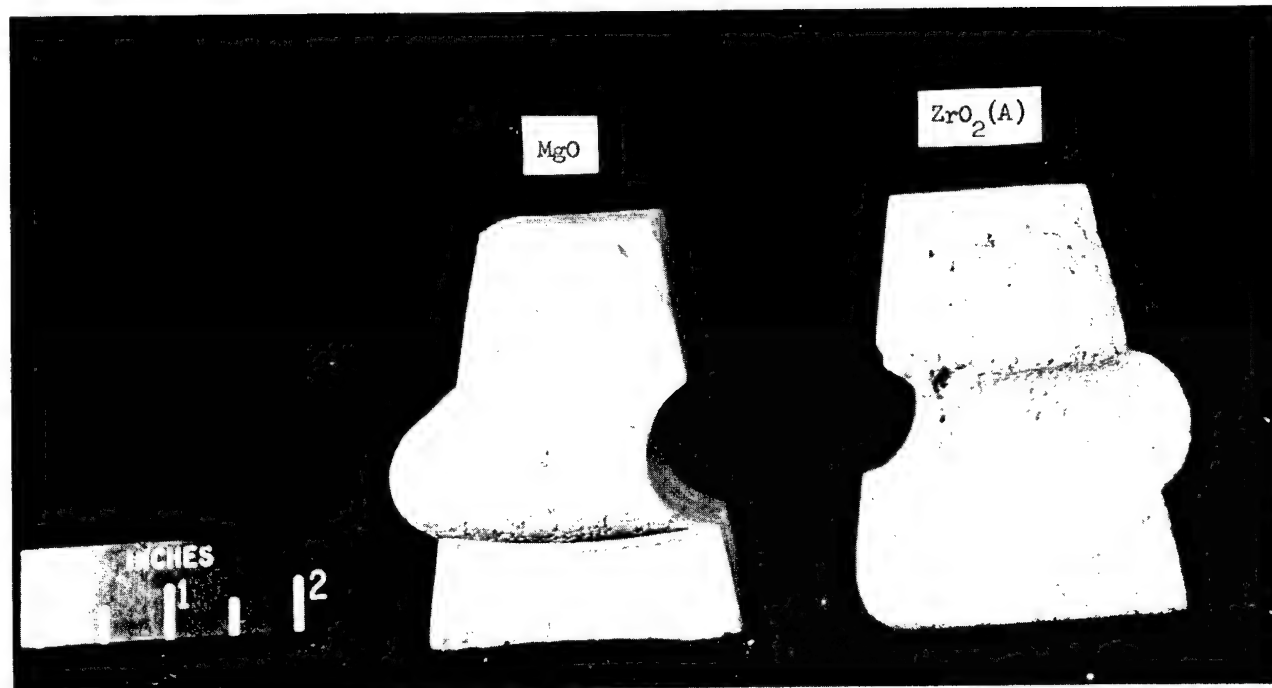


Figure 18.- Melting temperature as compared with interface contact temperatures of selected high-temperature refractory material. Interface loading approximately 0.3 pound per square inch.



(a) View of bricks as arranged for test.

L-62-4469.1



(b) View of reacting surfaces.

L-62-4463.1

Figure 19.- Reaction between zirconia A and magnesia bricks under 10 pounds per square inch loading at 3500° F.

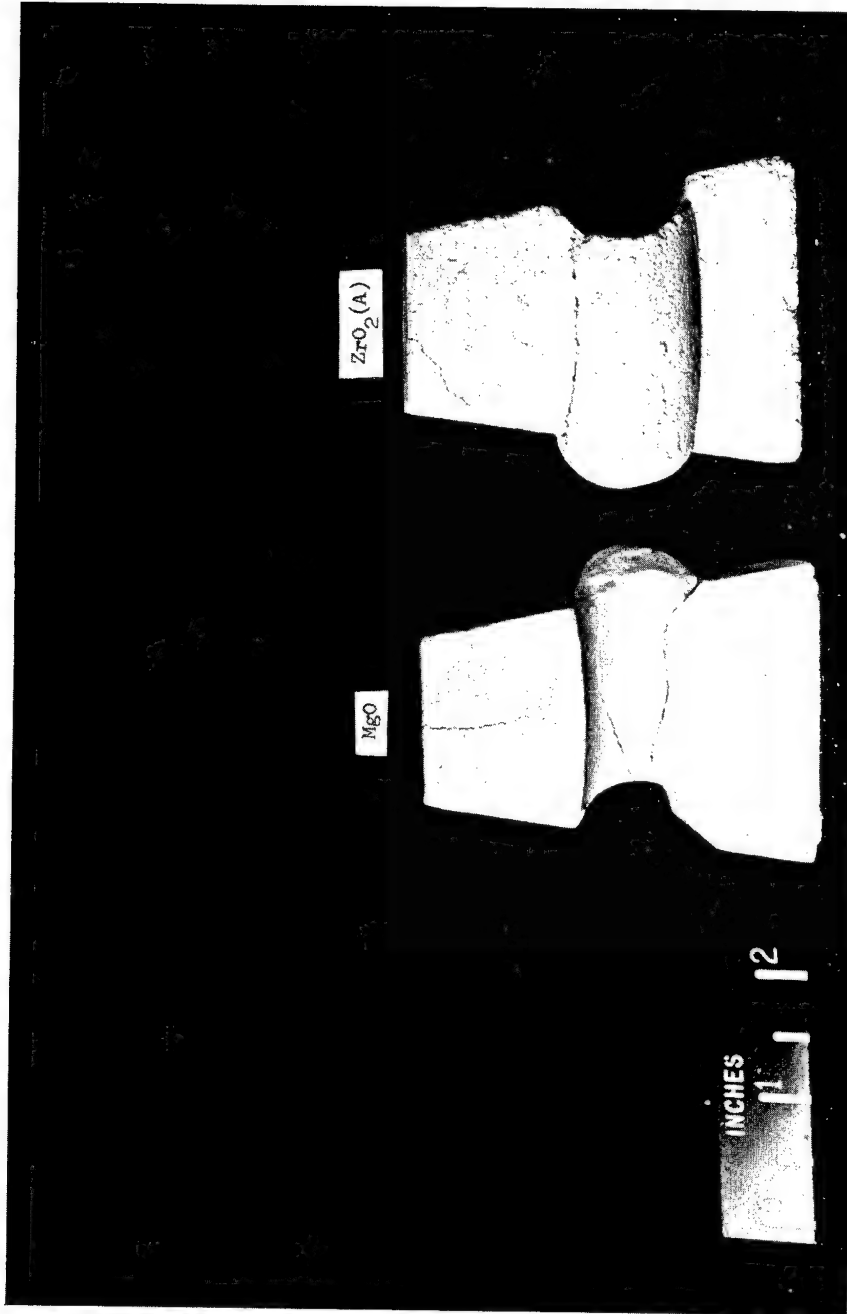
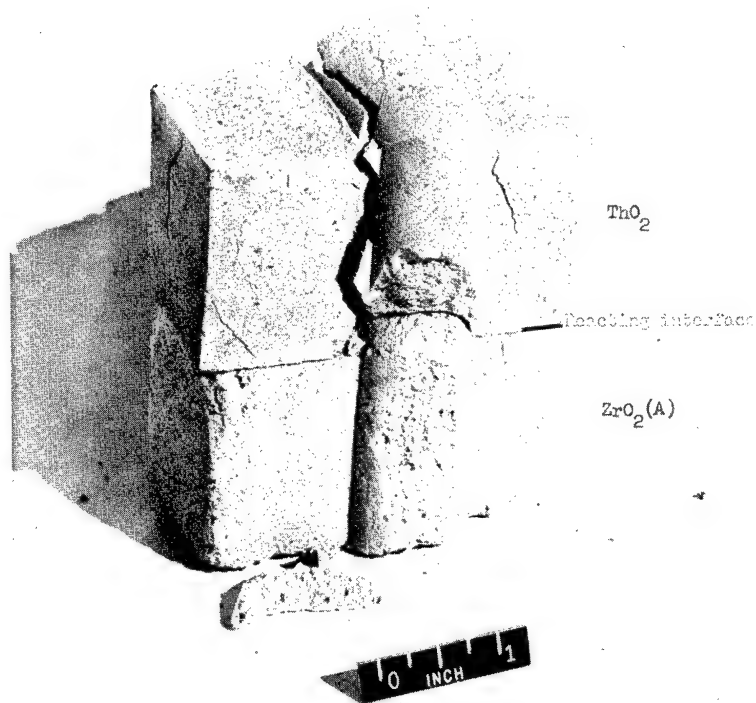
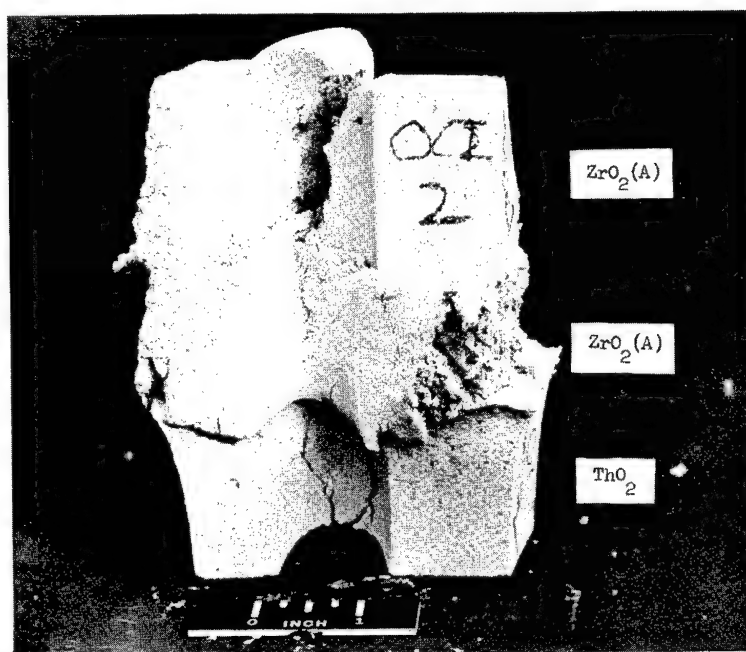


Figure 20.- Reaction between zirconia A and magnesia bricks under 10 pounds per square inch loading at 3100° F for 8 hours. L-62-4464.1



(a) No-load condition.

L-59-6522.1



(b) Under 4 pounds per square inch loading. L-59-7447.1

Figure 21.- Reaction between zirconia A and thorium bricks at 4000° F.

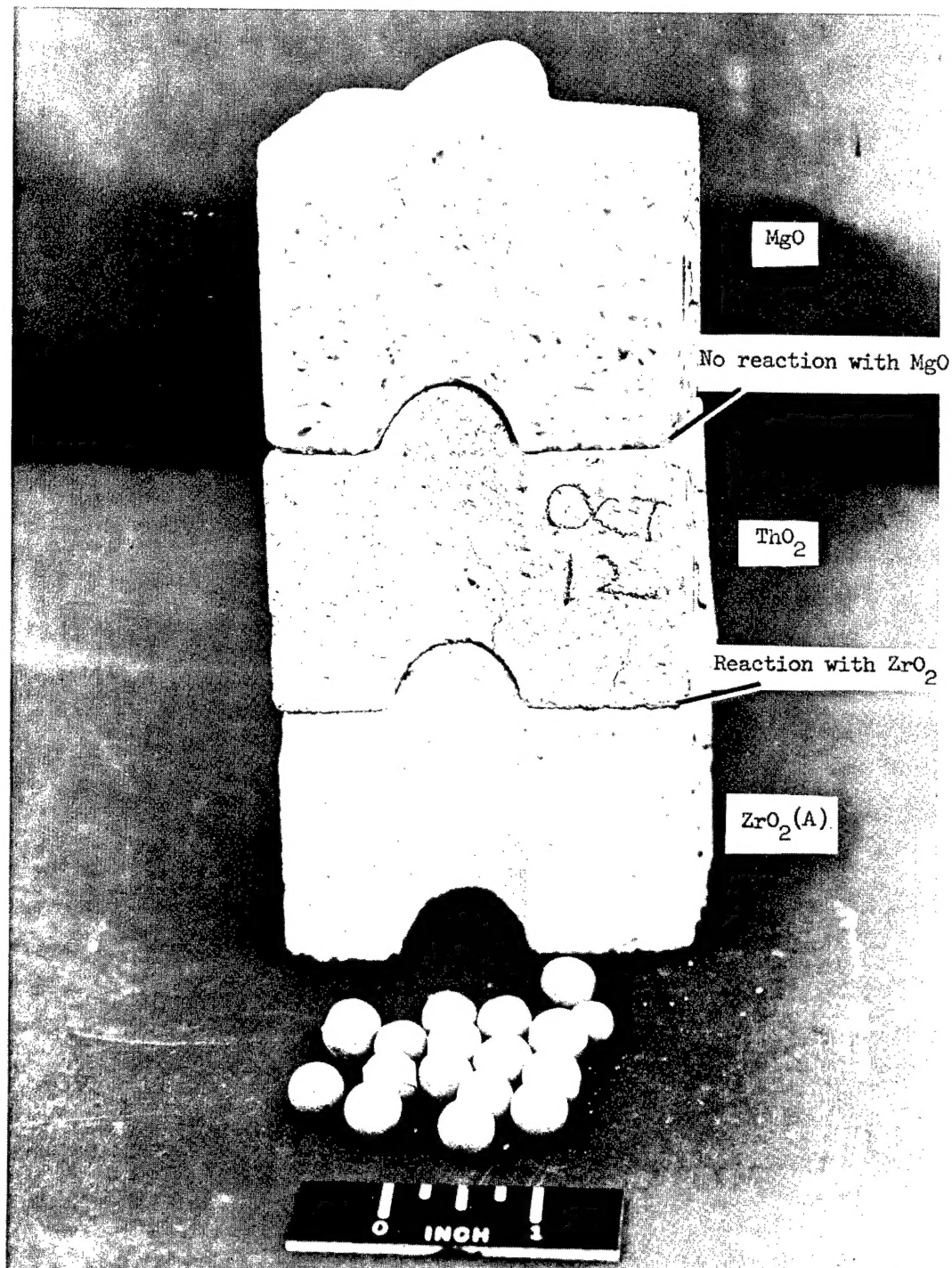


Figure 22.- Bricks after tests for reaction of thorium with magnesia and zirconia A at 3800° F without load.





NASA TN D-2493  
National Aeronautics and Space Administration.  
EVALUATION OF SELECTED REFRACTORY OXIDE  
MATERIALS FOR USE IN HIGH-TEMPERATURE  
PEBBLE-BED WIND-TUNNEL HEAT EXCHANGERS.  
John D. Buckley and Bennie W. Cocke, Jr.  
September 1964. 30p. OTS price, \$0.75.  
(NASA TECHNICAL NOTE D-2493)

Results are presented from laboratory tests and heat-exchanger experience comparing the properties of some refractory materials available for use in pebble-bed heat exchangers. Qualitative data on properties such as thermal-shock resistance and static load capacity at temperatures between 3000° F and 4000° F are presented for several types of zirconia, for thoria, and for magnesia. Based on these results and heat-exchanger experience, certain refractory materials are recommended for use in the several temperature zones of a heat exchanger.

NASA

- I. Buckley, John D.
- II. Cocke, Bennie W., Jr.
- III. NASA TN D-2493

NASA TN D-2493  
National Aeronautics and Space Administration.  
EVALUATION OF SELECTED REFRACTORY OXIDE  
MATERIALS FOR USE IN HIGH-TEMPERATURE  
PEBBLE-BED WIND-TUNNEL HEAT EXCHANGERS.  
John D. Buckley and Bennie W. Cocke, Jr.  
September 1964. 30p. OTS price, \$0.75.  
(NASA TECHNICAL NOTE D-2493)

Results are presented from laboratory tests and heat-exchanger experience comparing the properties of some refractory materials available for use in pebble-bed heat exchangers. Qualitative data on properties such as thermal-shock resistance and static load capacity at temperatures between 3000° F and 4000° F are presented for several types of zirconia, for thoria, and for magnesia. Based on these results and heat-exchanger experience, certain refractory materials are recommended for use in the several temperature zones of a heat exchanger.

NASA

- I. Buckley, John D.
- II. Cocke, Bennie W., Jr.
- III. NASA TN D-2493

NASA TN D-2493  
National Aeronautics and Space Administration.  
EVALUATION OF SELECTED REFRACTORY OXIDE  
MATERIALS FOR USE IN HIGH-TEMPERATURE  
PEBBLE-BED WIND-TUNNEL HEAT EXCHANGERS.  
John D. Buckley and Bennie W. Cocke, Jr.  
September 1964. 30p. OTS price, \$0.75.  
(NASA TECHNICAL NOTE D-2493)

Results are presented from laboratory tests and heat-exchanger experience comparing the properties of some refractory materials available for use in pebble-bed heat exchangers. Qualitative data on properties such as thermal-shock resistance and static load capacity at temperatures between 3000° F and 4000° F are presented for several types of zirconia, for thoria, and for magnesia. Based on these results and heat-exchanger experience, certain refractory materials are recommended for use in the several temperature zones of a heat exchanger.

NASA

- I. Buckley, John D.
- II. Cocke, Bennie W., Jr.
- III. NASA TN D-2493

NASA TN D-2493  
National Aeronautics and Space Administration.  
EVALUATION OF SELECTED REFRACTORY OXIDE  
MATERIALS FOR USE IN HIGH-TEMPERATURE  
PEBBLE-BED WIND-TUNNEL HEAT EXCHANGERS.  
John D. Buckley and Bennie W. Cocke, Jr.  
September 1964. 30p. OTS price, \$0.75.  
(NASA TECHNICAL NOTE D-2493)

Results are presented from laboratory tests and heat-exchanger experience comparing the properties of some refractory materials available for use in pebble-bed heat exchangers. Qualitative data on properties such as thermal-shock resistance and static load capacity at temperatures between 3000° F and 4000° F are presented for several types of zirconia, for thoria, and for magnesia. Based on these results and heat-exchanger experience, certain refractory materials are recommended for use in the several temperature zones of a heat exchanger.

NASA

- I. Buckley, John D.
- II. Cocke, Bennie W., Jr.
- III. NASA TN D-2493

*"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."*

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

## NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

**TECHNICAL REPORTS:** Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

**TECHNICAL NOTES:** Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

**TECHNICAL MEMORANDUMS:** Information receiving limited distribution because of preliminary data, security classification, or other reasons.

**CONTRACTOR REPORTS:** Technical information generated in connection with a NASA contract or grant and released under NASA auspices.

**TECHNICAL TRANSLATIONS:** Information published in a foreign language considered to merit NASA distribution in English.

**TECHNICAL REPRINTS:** Information derived from NASA activities and initially published in the form of journal articles.

**SPECIAL PUBLICATIONS:** Information derived from or of value to NASA activities but not necessarily reporting the results of individual NASA-programmed scientific efforts. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

*Details on the availability of these publications may be obtained from:*

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
Washington, D.C. 20546